

# Readout

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## Analytical Solutions in Megatrends





HORIBA contributes with its analytical and measurement technology in three areas that lead megatrends: “energy and environment,” “biotechnology and healthcare,” and “advanced materials and semiconductors. In this issue, we introduce our analysis solutions for these three areas.



In search of a refreshing breeze blowing through the trees, I visited the highlands of Shinshu. As I strolled through the greenery, the sunlight filtering through the trees made me feel as if I had wandered into the world of an impressionist painting.

*-Photographer MATSUI Hideo-  
(Member of Nikakai Association  
of Photographers)*

#### *Name of this Journal*

This Journal is named “Readout” in the hope that “the products and technology we have created and developed will be read out and so become widely known”.

## Analytical Solutions in Megatrends

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## HORIBA's Global Analysis Services for Megatrends



### KOMATANI Shintaro

Junior Corporate Officer  
General Manager  
Analytical Technology Division  
HORIBA Techno Service Co., Ltd.  
Ph. D.



In recent years, the environment surrounding us has reached a major turning point in terms of energy issues associated with population growth, responses to environmental pollution, medical care to support people's health, and work style reforms.

These social changes are driving innovations in technology, and the roles and expectations of companies in research, development and production are increasing, including the penetration of a digital society, advanced medicine such as gene therapy, and carbon neutrality in the shift to clean energy.

HORIBA has recognized this social trend and will further strengthen its partnership with customers by accelerating the development of analysis and measurement applications based on HORIBA's unique instruments, technologies, and know-how, creating new analysis and measurement solutions, and supporting research and development as "measurement" technology, in addition to the conventional product sales.

### Aiming to create new values for "measurement" technology on a global scale

On the other hand, looking around the world, approaches to social issues differ from country to country and from region to region due to differences in national policies and regional characteristics.

HORIBA has 18 analysis laboratories around the world, each equipped with its own analysis and measurement instruments.

These laboratories not only conduct demonstrations for conventional instrument sales and test analysis by customer development teams, but also develop new analytical methods based on "Measurement" technology, provide contract analysis and testing, and conduct joint research with companies, universities, and other

research institutions. We have established a system that enables us to develop applications and provide analysis/measurement solutions tailored to the needs of each region.

Therefore, the name has been changed from “HORIBA Analysis Center” to “Analytical Solution Plaza,” and its role has been clarified and sharpened to accelerate activities as a place where analysis professionals gather to create new analysis and measurement value and provide solutions unique to HORIBA to meet the diverse needs of our customers.

Here is an example of our participation in the “Hayabusa2” project at the Analytical Solution Plaza in Japan and our challenges based on “Measurement” technology.

In December 2020, JAXA’s asteroid explorer “Hayabusa2” brought back sand from the asteroid Ryugu, and in June 2021, its initial analysis confirmed that Ryugu is an asteroid with a composition similar to the average elemental composition of the solar system, rich in organic carbon, and carbonates produced by structural water and water quality denaturation were found. We participated in this project, which required the analysis of precious samples with unprecedentedly small amounts, and developed and proposed optimal analytical principles and methods, sampling methods, pretreatment, jigs and analysis techniques, while conducting elemental analysis using an X-ray fluorescence microscope (XGT-9000), confirmation of carbonates using a Raman microscope (LabRAM), quantitative analysis of carbonates and organic substances using the new carbon and sulfur analysis system in materials (EMIA-STEP). With these sample handling processes, we were able to provide one-of-a-kind analysis and measurement solutions by creating new value for existing analysis and measurement problems.

In this way, we will continue to support our customers’ R&D and other corporate activities based on “measurement” technology, not only by selling instruments and existing analysis and measurement solutions, but also by creating new applications, even in an era of change.

We not only develop analytical and measuring instruments based on new analytical principles and existing technologies, but also create new value in analysis and measurement, including the development of application technologies such as analytical methods and software, as well as solutions that ensure the reliability and safety of analytical data. We will continue to pursue our mission as a partner that can provide high value-added solutions to our customers.

HORIBA will continue to meet the expectations of our customers with our “measurement” technology, from research and development to analysis and measurement in manufacturing and quality inspection lines.

In this Readout No. 56, we will introduce our new Analytical Solution Plaza, a facility designed to provide customers with solutions based on “measurement” technology, as well as our efforts to provide analytical solutions at our domestic and overseas locations based on three business fields that we focus on ; “Energy & Environment,” “Materials & Semiconductor,” and “Bio & Healthcare”.

We promise that HORIBA’s analytical technologies will continue to bring new value through close collaboration with our customers around the world.

\* Editorial note: This content is based on HORIBA’s investigation at the year of issue unless otherwise stated.

## Frontiers and Standardization Trends of Particle Measurement and Analysis Technology

### FUJIMOTO Toshiyuki

Chief Standardization Officer, Councilor  
Marketing and Business Development Headquarters  
National Institute of Advanced Industrial Science and Technology  
Doctor of Science



This report summarizes the frontiers of measurement and analysis technologies related to particle size, which is a fundamental and extremely important Physico-chemical property of fine particles, with a focus on compliance with regulations in Europe, where leading technical standards are being introduced, as well as recent topics in standardization. In the case of particle size measurement in air, the calibration of detectors, which is directly related to the regulations, and in the case of particle size measurement in liquid, the number-based size distribution, which is the basis of the EC definition of nanomaterials, were introduced, including attempts to obtain international equivalence by using various measurement methods.

### Introduction

The specific properties of atomic and molecular ensembles have been used for a long time. It is not easy to identify the beginning, but it is widely known that some stained glass elements that had a great influence on medieval European architecture use fine particles of color.

As the progress of measurement and analysis techniques has led to reports that fine particles exhibit properties that differ from those of their atomic (microscopic) and bulk (macroscopic) constituents, along with their size, research and development in the area of mesoscopic science and cluster science have been actively promoted for the understanding and active use of these characteristics.

Many effects of size on properties in both chemical and physical fields have been reported, for example, the catalytic activity of platinum particles varies depending on particle size, and the effects of size on the properties have been noted. In addition to composition and structure, the importance of size (spatial spread) parameters have been highlighted. The concept of nanotechnology was proposed in the mid-1970s for the expression and application of new physical and chemical properties based on size. Since then, research and development on nanotechnology has been promoted in various countries, starting with the National Nanotechnology Initiative in the United States, and many products using nanotechnology are now found

around the world. On the other hand, there is a need to establish reliable particle size measurement and analysis techniques, as there is also a demand to evaluate the effects of specific physical and chemical properties that are based on size on health and the environment.

In this report, the trend of standardization is outlined, focusing on measurement technology to obtain accurate particle size and distribution.

### Definition of nanomaterials in Europe

On June 10 2022, the European Commission (EC) issued a final recommendation<sup>[1]</sup> on the definition of nanomaterials. The recommendation amends the official definition of nanomaterials for use in regulations (2011/696/EU) issued in 2011. While ISO had previously specified the size and structure of individual objects (ISO/TS8004-1), the EC definition includes the size range and distribution of the number of objects in a specific quantity, which is a more advanced definition when dealing with real materials. However, the difficulty in determining the size distribution including the constituent particles of the aggregate has caused confusion to both material manufacturers and measurement experts. For the effective use of nanomaterials definition, large-scale projects such as NanoDefine were promoted in the European Union (EU) and an intensive research was conducted by the Joint Research Center (JRC) of the EC. The final recommendations, which have improved the practicality based on the findings obtained

through them, are as follows. The full definition of new nanomaterials is quoted below, considering the possibility of their use in various regulations in the future.

- (1) ‘Nanomaterial’ means a natural, incidental or manufactured material consisting of solid particles that are present, either on their own or as identifiable constituent particles in aggregates or agglomerates, and where 50% or more of these particles in the number-based size distribution fulfil at least one of the following conditions:
- (A) one or more external dimensions of the particles are in the size range 1 nm to 100 nm.
  - (B) the particle has an elongated shape, such as a rod, fibre or tube, where two external dimensions are smaller than 1 nm and the other dimension is larger than 100 nm;
  - (C) the particle has a plate-like shape, where one external dimension is smaller than 1 nm and the other dimensions are larger than 100 nm.

In the determination of the particle number-based size distribution, particles with at least two orthogonal external dimensions larger than 100 µm need not be considered.

However, a material with a specific surface area by volume of  $< 6 \text{ m}^2/\text{cm}^3$  shall not be considered a nanomaterial.

- (2) For the purposes of point (1), the following definitions apply:
- (A) ‘particle’ means a minute piece of matter with defined physical boundaries; single molecules are not considered ‘particles’
  - (B) ‘aggregate’ means a particle comprising of strongly bound or fused particles
  - (C) ‘agglomerate’ means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual

## Measurand and measurement procedure

In the report published by JRC in 2012 titled “Measurement methods required to implement EC Definitions for Nanomaterials”,<sup>[2]</sup> the currently used particle size measurement methods are classified into three categories: ensemble methods (DLS, SAXS, etc.) to obtain overall information on a certain amount of sample as the size measurement method of nanoparticles, counting methods (TEM, SEM, AFM, etc.) to measure each component separately, and fractionation methods (FFF, CLS, SEC, etc.) to evaluate each size of separated fractions. The introduction of the classification is an excellent analysis of measurement methods. Based on the characteristics of each

method, the use of multiple measurement techniques will not only enable the acquisition of the necessary information accurately, but will also enable new analytical evaluations. It is important to accurately grasp and understand the applicability and the measured values.

Even if the same particle size is measured, the details of the measured quantity often vary depending on the method used (method dependent). The main reason for the method dependence is the difference in the physical phenomena used. In order to compare the results of counting nanomaterials individually with the results of evaluating them as averaged value in a space (ensembles), it is necessary to examine the details of each measurement principle. Furthermore, even with the same counting method, there is a difference (Method dependent), for example, the equivalent circle diameter in TEM and the electric mobility equivalent sphere diameter obtained by DMAS. By utilizing the difference in measurement quantity, applications such as obtaining a quantitative index of particle shape from the relationship between mean particle diameter and particle size distribution can be expected.

Moreover, it is known that the results of the same measurement method differ according to the measurement procedure (protocol dependent). The main reason for the procedural dependence is that the quantity of measurement actually detected depends on the measurement parameters. For example, when the palm is slowly immersed in the water, this action may cause the hand to feel mainly water temperature or water viscosity. If the palm of the hand was used to hit the surface of the water quickly, the main sensation of the hand would be the surface tension of the water. This means that simply changing the speed of movement of the hand used for detection (measurement parameters) has changed the amount of measurement detected (physical quantity).

It is paramount to consider the physical phenomena used, the measurement procedures applied, and the condition of the object, and to ensure that the instrument is properly calibrated and that the measurement procedures are validated in order to achieve accurate measurement analysis of particle sizes.

## Airborne particle measurement and standardization trends

The state in which tiny particles are suspended in the gas phase is called an aerosol. In particular, the composition, size, and quantity of particulate matter suspended in the air have been monitored for a long time from the viewpoint of environmental protection and occupational safety. Measurements of large particles, such as PM<sub>2.5</sub>, are

carried out by using inertial forces to remove coarse particles using impactors or cyclones, and then by collecting particles from a constant volume of the atmosphere with a filter and evaluating their mass. The particulate concentration evaluated by these methods is expressed as mg/m<sup>3</sup> and is called the mass concentration. Together with the idea that the toxicity of particles increases with the total mass of the exposed particles, the aerosol of large particles is better evaluated by mass, and the European automobile emission regulations for particulate matter were limited to mass standards only until Euro5 in 2009. As the amount of particulate matter contained in exhaust gases decreased due to the advancement of material collection technology, it became necessary to evaluate the quantity standards for monitoring more dilute particles. Introduced in 2011, Euro5<sup>+</sup> introduced a number standard in addition to the mass standard for particulate matter in diesel exhaust emissions. The number of solid particles in the exhaust gas is measured by the particle counter after removing the volatile component particles by heating dilution. The Condensation Particle Counter (CPC) is usually used as a particle counter.

In principle, CPC has an excellent property to provide stable detection efficiency for a wide range of particle sizes, but with decreasing particle size, the detection efficiency decreases rapidly. This is mainly due to insufficient particle growth due to the adsorption of atmosphere molecules onto the surface of the fine particle at the lower detection limit. For this reason, the detection efficiency of particles near the lower limit of detection is specified for use in regulation. The detection efficiencies of the particles regulated in Euro5<sup>+</sup> /Euro6 and planned to be introduced in Euro7 are shown in Table 1.

Table 1 Requirements of particle detection efficiencies under European vehicle emissions controls

Year	Particle Detection Efficiencies
Euro5 <sup>+</sup>	50% ± 12% @ 23 nm Over 90% @ 41 nm (SPN23)
Euro6	
Euro6a	
Euro7	65% ± 15% @ 10 nm Over 90% @ 15 nm (SPN10)

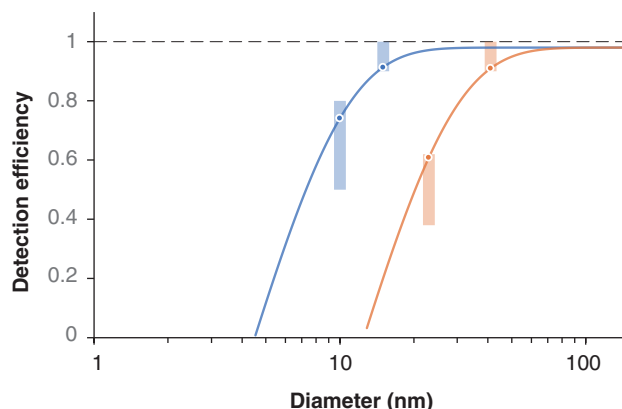


Figure 1 Requirements of particle detection efficiencies under European vehicle emissions control (indicated by bands) and typical detection efficiency curves of a CPC. Orange is for SPN23, blue is for SPN10 (planned).

It should be noted that Euro7, which is scheduled to be introduced in 2025, is considering extending the lower limit from the number of solid particles with a particle size of 23 nm or greater to the number of solid particles with a particle size of 10 nm or greater.

Figure 1 shows each demand value (indicated by band) and a typical CPC detection efficiency curve. Both SPN23 and SPN10 require advanced calibration to meet the required values.

The uncertainty of the detection efficiency calibration of CPC and the standard Faraday-cup aerosol electrometer has already been reported.<sup>[3]</sup> Figure 2 shows the general calibration scheme of CPC.

In the particle generator, it is necessary to generate a stable number of particles at the target particle size. The electro-spray method, which generates small and uniform sized droplets, is often used for particle generation. When using a capillary with an inner diameter of 25 μm, the droplet diameter is about 150 nm to 200 nm. In the calibration of detection efficiency of CPC for measuring automobile exhaust emissions, poly- $\alpha$ -olefin (Pole- $\alpha$ -Olefin:PAO) dissolved in alcohol is usually used. The detection efficiency of CPC is also affected by the chemical properties of the particles, especially near its lower limit. PAO, a hydrocarbon, can be expected to provide detection efficiency comparable to that of particulates in automobile exhaust gas. By adjusting the concentration of PAO solution, the size of PAO particles after the evaporation of alcohol solvent can be controlled.

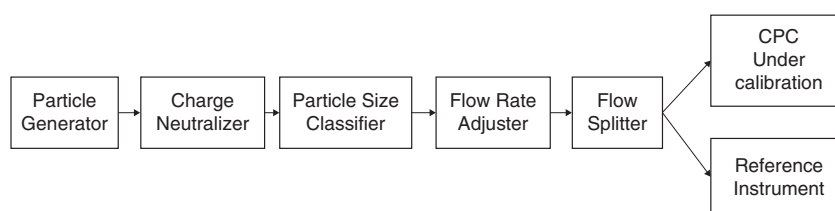


Figure 2 Schematic representation of the CPC calibration setup.



The droplet is electrically neutralized and the solvent-volatilized particles are monodispersed to the size used for checking the detection efficiency in the Particle Size Classifier. The solvent evaporation must be completed and the particle size must be stable before it is introduced into the particle size fractionator, and the verification is one of the key factors for accurate detection efficiency. The differential mobility analyzer (DMA) is used for the particle size fractionator. Since the particle size value in the device is the horizontal axis of Figure 1, it is necessary to fully understand and minimize the uncertainty. Based on a detailed analysis of the uncertainty of the DMA particle size calibration, the AIST has been examining the supply of DMA size calibration with sufficient uncertainty from both the calibration with DMA reference equipment and the calibration via the reference material.

Recently, the miniaturization and uniformity of droplets generated from inkjet nozzles has dramatically improved due to the demand for improved print quality. The inkjet technology capable of producing minute and uniform droplets has been widely applied in various fields such as pharmaceutical manufacturing. It is also widely used in the field of measurement analysis for examples, sample preparation by ICP-MS, ionization of samples, and spray drying method.

The Inkjet Aerosol Generator (IAG) is being developed to establish a single dispersion particle count standard.<sup>[4]</sup> In order to utilize this method, it is necessary to study the stability of the produced nuclei and the precipitation of impurities in the nucleation, which is caused by the increase of the contamination opportunity of the solution due to the complicated path, especially when generating small particles.

Since the number of particles generated in IAG can be controlled digitally, it is possible to calibrate the detection efficiency by directly connecting the IAG and CPC in the grain size region where the size, stability and reproducibility of the particles produced are sufficiently evaluated. IAG has already been used to calibrate an OPC(Optical Particle Counter). ISO 21501-4, Determination of particle size distribution - Single particle light interaction methods - Part 4: light scattering airborne particle counter for clean spaces is currently being developed in ISO/TC 24/SC 4 and will be added to the IAG as one of the calibration methods. As of July 2022, the addendum is in DAMD state, but will be issued as Amd in 2023.

The use of IAG greatly simplifies the calibration set-up of Figure 2, and it is expected that a calibration system with increased portability will be developed depending on the required measurement conditions and accuracy, and that a

standard embedded measurement system with a calibration system built into the measurement system will be realized.

In addition, IAG is expected to use biomaterials and markers in the solution as a reference for the composition and functionality of the particles produced.

## Dispersed particles in liquid and standardization trends

The measurement and analysis methods of dispersed particles in liquid vary widely, including the measurement method of dispersed particles on solid surfaces. For this reason, differences in measurement results due to the differences in measurement volume described in Chapter 3 are often considerable. JRC published a report<sup>[5]</sup> in 2019 as points to consider in the assessment of particulate materials according to the European Commission's Recommendation on a definition of nanomaterial. The report includes results of evaluating particle sizes using various methods for European reference materials with different dispersion properties. It is reported that the difference between the measurement methods is small for samples with spherical particles close to monodisperse, whereas the difference between the measurement methods is significant for samples with large particle size distributions. This is because the underlying physical principle of each measurement usually only works for ideal sample systems with monodisperse particle sizes.

In real materials, due to the spread of the particle size distribution, attention must be paid to realize a reliable measurement and analysis of particle size. Results of DLS and LD, the typical ensemble methods for samples with bimodal particle sizes, are introduced. The sample used is a 1:1 (mass based) mixture of PSL (PolyStyrene Latex) standard particles with a particle size of 70 nm and 180 nm. SEM images of each PSL standard particle are shown in Figure 3.

It is shown that both PSL particles are spherical and have extremely sharp particle size distribution. Given that the density of PSL is constant regardless of particle size, there

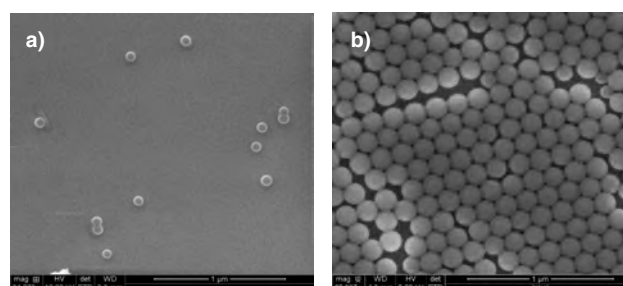


Figure 3 Electron micrographs of PSL reference particles. a)  $d = 70$  nm, b)  $d = 180$  nm

are about 17 times as many 70 nm PSL particles in the mixed solution adjusted at a mass ratio of 1:1 as there are 180 nm PSLs on number basis.

Figure 4 shows the particle size distribution of particles in mixed solutions evaluated by DLS and LD. In Figure 4, a unit of vertical axes of two measurements is different, but the size distribution of the two peaks cannot be reproduced in both measurements. This is because the intensity of the light scattered from the particles is proportional to the sixth power of the particle size, so strong scattered light from large particles can shield the effect of weak scattered light from small particles.

Although DLS and LD have excellent features as ensemble methods, for accurate analysis of materials with wide particle size distribution, it is necessary to compose the results obtained by dividing them into multiple fractions with narrow particle size distribution. A case has been reported that the combination of Field-Flow Fractionation and DLS reproduce a particle size distribution of bimodal samples adequately.<sup>[6]</sup>

As the definition of nanomaterials in EC is based on the size distribution of the particles on a number basis, verification of the reproducibility of measurements across laboratories and countries for number-based concentrations is being conducted in various frameworks. The largest case is a comparison of gold nanoparticle number concentrations between laboratories conducted by the Versailles project on Advanced Materials and Standards (VAMAS), with the participation of 50 research institutions from around the world.<sup>[7]</sup> A gold nanoparticle with a particle size of 30 nm dispersion in water was used for the sample. Preliminary studies by CLS and SEM showed that the gold nanoparticles stabilized by citric acid of the sample are almost spherical and have very narrow particle size distribution. Measurement methods used for comparison were SAXS, CLS, UV-Vis, PTA, and spICP-MS. The

results was discussed by comparing the counting method (PTA and spICP-MS) and population-averaging methods (SAXS, UV-Vis and CLS).

What is interesting about the results is that the population-averaging method shows high reproducibility between laboratories. The relative standard deviations of SAXS, CLS, and UV-Vis reported were 2.6%, 11%, and 1.4%, respectively. The Ensemble method, in particular, showed high reproducibility in the evaluation of the sample at the ideal number concentrations, beyond the laboratory. This is attributed to the relatively simple and robust measurement set-up and a measurement protocol of the method. CLS is considered technically more complicated and requires more detailed calibration. In contrast, the reported inter-laboratory reproducibility of the counting method were significantly lower than those by a population-averaging method. Inter-laboratory reproducibility of the spICP-MS and PTA are 46% and 68%, respectively, whilst an intra-laboratory reproducibility of those are about 12% in relative standard deviation. The reason for the poor reproducibility between laboratories was considered including the effect of the dilution process at a sample preparations, but no clear interpretation has been reached. In order to improve the inter-laboratory reproducibility by counting method, it has been pointed out that standardization of the measurement and data processing procedures including sample preparation is important. In framework of the meter convention, pilot studies and international key comparisons using monodisperse gold nanoparticle dispersants and bimodal gold nanoparticle dispersants are being carried in the CCQM (Consultative Committee for Amount of Substance : Metrology in Chemistry and Biology). It is expected that a metrology and analysis base with higher accuracy and international consistency for the number concentration measurement of nanoparticles will be established.

The international standardization of particulate measure-

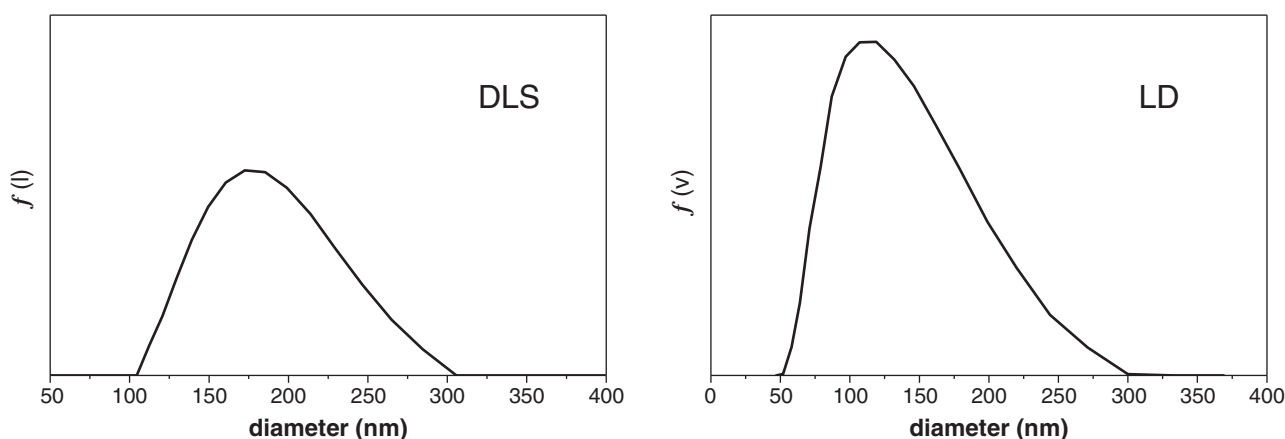


Figure 4 Particle size distributions of bimodal reference sample evaluated by DLS and LD. DLS(Dynamic Light Scattering), LD(Laser Diffraction)

ment and analysis is mainly carried out in the ISO TC 24/SC 4 or ISO TC 229/JWG 2 (for AFM measurement techniques, ISO TC 201/SC 9). The PTA and spICP-MS methods, which are important for measurement and characterization of a number-based size distributions of nanoparticle, already have international standards (ISO 19430:2016, ISO/TS 19590:2017, respectively). Both have been updated on a regular basis and are currently undergoing revisions with recent technical progresses.

At the usage of counting method for particle number concentration, PTA has a higher potential to simplify a measurement protocol by automation, compared to the microscopic method. It is expected that the PTA can be

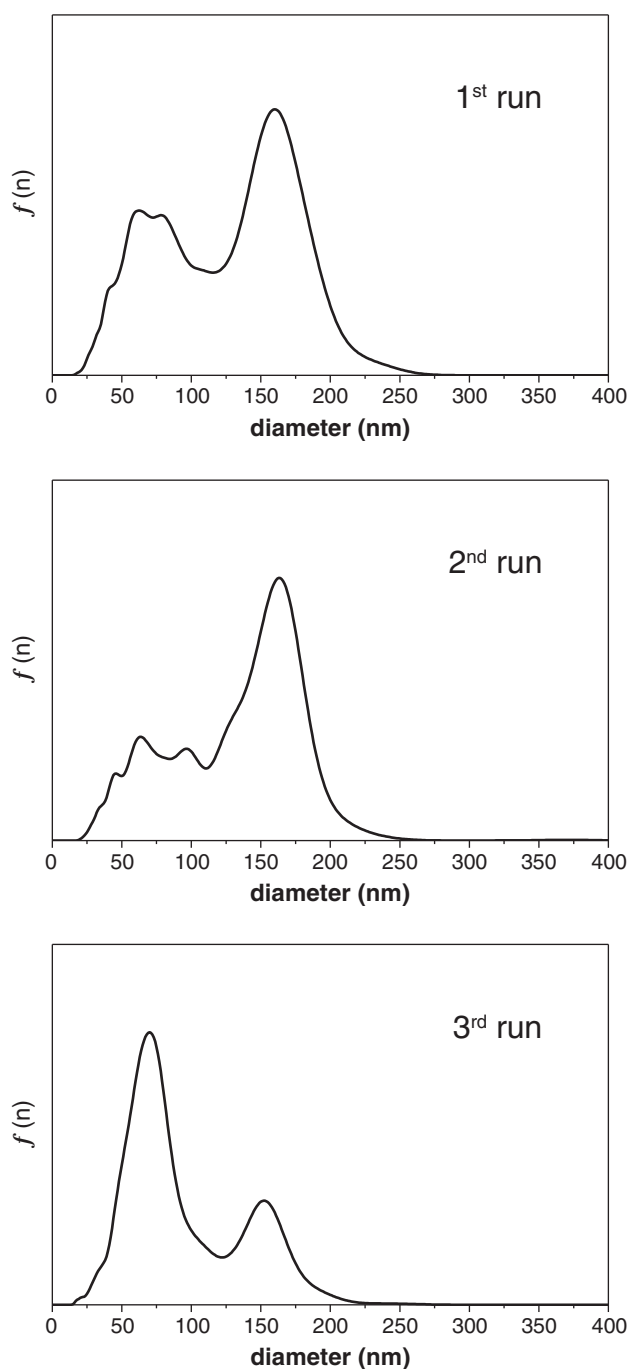


Figure 5 Number based particle size distribution evaluated by PTA method for a bimodal reference sample.

applied to a in line usage.

Figure 5 shows measurement results of a mixture of the standard particles of PSL with a particle size of 70 nm and 180 nm with a mass ratio of 1:1 by PTA.

The size distribution shows that it is bimodal, but the concentration axis varies from measurement runs. Particle size distribution by single run does not reflect the number concentration at the preparation. Since the particles in an area to measure by PTA is far fewer than the whole sample as similar in other microscopic methods, it is important to confirm that the data accumulation is statistically significant as in other microscopy methods.

The selection of specific surface areas is first used to determine the conformity of EC to the nanomaterials definition, but if the final decision is doubtful, measurement analysis by an electron microscope is required to confirm the constituent particles of the aggregate. In the use of electron microscopes, it is necessary to use statistically correct standardized procedures for the sample preparation and the analysis of results. ISO 21363:2020 (Nanotechnologies - Measurements of particle size and shape distributions by transmission electron microscopy) can be used for TEM, and ISO 19749:2021 (Nanotechnologies - Measurements of particle size and shape distributions by scanning electron microscopy) can be used for SEM. .

These international standards are also cited in OECD Test Guideline 125 (Nanomaterial Particle Size and Size Distribution of Nanomaterials, 30 June 2022).

## Conclusion

The recent topics on particle measurement/analysis technology and standardization were summarized, mainly in response to European regulations, where leading technical standards are introduced. Since 2011, when the first edition of the definition of nanomaterials was proposed by EC, the detailed understanding of particulate measurement/analysis and the improvement in the reliability of the measurement results have been remarkable.

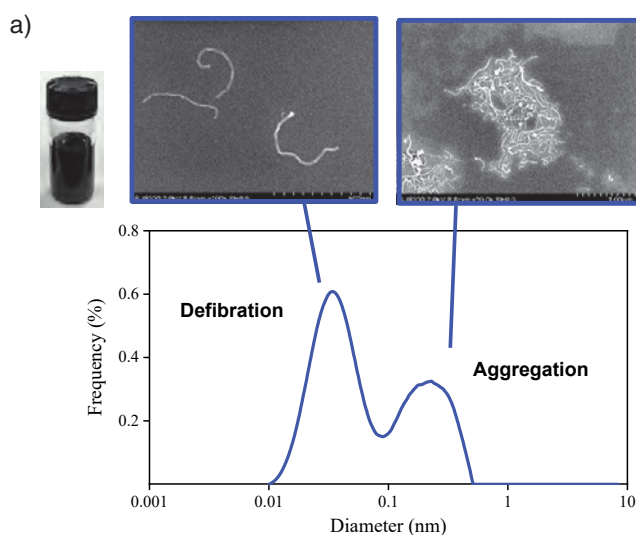
In 2021, AIST has established a cooperative research laboratory, HORIBA Institute for Particle Analysis in AIST TSUKUBA(HIPAA), in the national metrology institute of Japan (NMIJ). Major aims of the HIPAA is to develop a world leading particle measurement systems and put them into practical use. The activity has been started with the themes of developing a particle measurement system to comply with stricter environmental regulations, and an analysis and evaluation system for nanomaterial charac-

teristics. In the development of particle measurement systems, an important knowledge is being obtained for the accuracy improvement and system simplification for smaller particles measurement in areas such as PM2.5 and automobile exhaust particles, where further tightening of regulations is expected in the future to solve environmental issues. On the other hand, in the development of a system for analysis and evaluation of nanomaterial properties, a detailed study using carbon nanotubes and cellulose nanofibers through comparisons with microscopic observation is being performed in order to establish reliable applications for centrifugal particle size distribution measurement systems. Results have been obtained that lead to high-resolution particle size analysis by centrifugal sedimentation, which is difficult to achieve with conventional scattering methods (Figure 6).

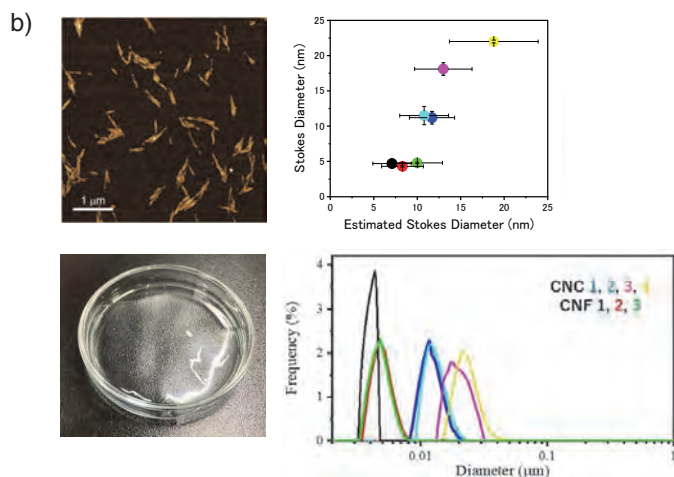
Furthermore, in promoting the utilization and practical application of these results, it is expected that results will be created to expand the fields of application by taking characteristics of the cross-disciplinary nature of particle measurement technology.

In recent years, DX (Digital Transformation) has been promoted worldwide, aiming to generate new knowledge by accumulating measurement and analytical data. The principle of FAIR (Findable, Accessible, Interoperable, and Reusable) has been proposed for sharing data that is important in DX. The details of FAIR principles have been discussed in various communities, but it is important that the data should be stored with sufficient metadata, accessible and understandable in standard ways, and that the traceability of the data is clearly described.

Application development of Centrifugal Nanoparticle Analyzer in HORIBA Institute for Particle Analysis in AIST TSUKUBA



a) Carbon Nano Tube : Particle size distribution and electron microscope images.



b) Nanocellulose: Particle size distribution and correlation with AFM.



Centrifugal Nanoparticle Analyzer

Since fine particles are used in a wide range of technical fields, information required for measurement and analysis of particles is diverse. Reliable shared data, stored and accumulated with sufficient metadata based on a detailed understanding of measurement and analysis techniques, is expected to lead to breakthrough applications of fine particles via DX. It is hoped that the use of excellent instrumentation and well-studied measurement protocols will enable cross-field interoperability of measurement results, leading to the understanding and utilization of noble characteristics of fine particles.

\* Abbreviation for measurement method

AFM(Atomic Force Microscopy),  
 CLS(Centrifugal Liquid Sedimentation),  
 CPC(Condensation Particle Counter),  
 DMA(Differential Electrical Mobility Analyzer),  
 DLS(Dynamic Light Scattering),  
 ICP-MS (Inductively Coupled Plasma – Mass Spectroscopy),  
 LD(Laser Diffraction),  
 PTA(Particle Tracking Analysis),  
 SAXS(Small-Angle X-ray Scattering),  
 SEM(Scanning Electron Microscopy),  
 spICP-MS(Single Particle ICP-MS),  
 TEM(Transmission Electron Microscopy),  
 UV-Vis(Ultra Violet - Visible)

\* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.

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## New Platform for Multimodal Spectroscopic Characterization of Semiconductors

Praveena MANIMUNDA

Francis NDI

Multimodal spectroscopy is the concept of combining several different spectroscopies onto one platform, thereby expanding the range of analytical capabilities available on that single platform. In advanced semiconductor fabrication, the need to streamline production and avoid unnecessary wafer handling makes it quite common to have several different metrologies at one wafer processing station. However, this concept is still not common at the material research or product & process development stages where it is more common to have several different instruments offering different analytical spectroscopies. Besides the obvious benefit of cost reduction, having multiple analytical spectroscopies offers the added benefit of sample co-location so that multiple complementary measurements can be made at the same location of the sample. The benefit of co-location is particularly important as feature sizes get smaller, from a few microns to nanometers in size. We show results from a multimodal microspectroscopy system from HORIBA for semiconductor characterization. The Standard Microscope Spectroscopy (SMS) system is a modular and flexible system capable of accommodating up to seven different spectroscopies, including Raman, Photoluminescence, Time-resolved Photoluminescence (Lifetime), Reflectance and Transmittance, etc. Furthermore, we show that even when there is a need to perform correlative measurements across different instruments, it is possible to use coordinate system transformation technologies, such as nanoGPS navYX™ from HORIBA to rapidly achieve sample co-location across different measurement platforms.

### Key words

multimodality, wafer handling, speed, cost minimization, reproducibility



## Introduction

Semiconductor devices are some of the most complex engineered devices in today's world. Their manufacture often requires an even more complex sequence of steps, first to understand and tailor the material properties so that desired electrical, optical or mechanical properties are possible, followed by very intricate and controlled fabrication processes so that devices are reproducible and reliable, and at a reasonable cost. The above sequence of events demands that the practitioner is able to measure the material and device properties at every step of the design and production process to ensure that yields are optimal, and to remove defective material or components as early as possible in the production process, as every step adds cost and complexity.<sup>[1]</sup> A vast number of techniques have been developed for these types of material, product and process characterization. Amongst these, optical or spectroscopic techniques are usually preferred. The preference for optical spectroscopy in semiconductor material and process characterization derives from several factors. Optical spectroscopic (OS) techniques are often non-contact, hence reducing the chances of contamination. Secondly, many OS techniques are comparatively fast and require little to no sample preparation.

Given the large number of material and process parameters that can affect the behavior of the final semiconductor product, it follows that control of the material design and fabrication process is necessarily a multimodal effort. This means that many measurement techniques are required to measure and control all the parameters that lead to desired device behavior. Instrument vendors have accordingly developed a wide variety of specialized optical spectroscopy instruments often specialized on each of the required techniques. In addition, as device features go from micro to nano, many of these instruments are based on a microscope or other submicron to nanometer measurement platform. For example, it is common in a semiconductor research or fabrication facility to have one micro-Raman spectroscopy instrument used to characterize crystallinity of epitaxial deposition or stress, and a separate photoluminescence instrument to measure wafer homogeneity, etc. Beyond the cost burden of having multiple instruments to perform these necessary measurements, the task itself, in going from instrument to instrument, has become quite challenging recently, as the features of interest become smaller and approach the micro to nanoscale.

In this article, we describe a novel approach to achieve multimodality on one microspectroscopy platform (Figure 1), enabling the practitioner to characterize various semiconductor samples using different spectroscopies



Figure 1 HORIBA multimodal, Standard Microscope Spectroscopy (SMS) system equipped with 12-inch wafer stage.

with the benefit of sample co-location. In this approach, various complementary measurements can be performed at the same micro location and in so doing, obtain deeper insights into the sample or process. In addition, when there is a necessity to perform micro or nano measurements across different instruments, we present a new coordinate transformation technology (nano-GPS) that enables fast and accurate location of nanostructures across different measurement instruments.

## Example 1: LEDs

One of the most important considerations of LEDs is the emission wavelength. For example, most common Lidar sources have semiconductor materials designed to have light emission at 905 nm or 1550 nm. The primary material property that controls this parameter is the optical bandgap, which is readily measured using micro photoluminescence (Figure 2a). After the material properties are understood, a fabrication process engineer could be

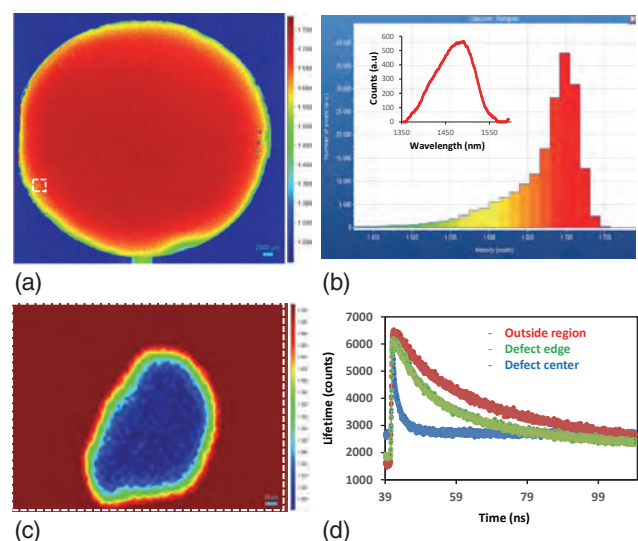


Figure 2 (a) Photoluminescence (PL) map on a InP wafer. (b) PL spectrum (insert) and histogram showing intensity distribution- an indication of homogeneity. (c) High resolution PL map on a defect region (dotted square on (a)). (d) PL lifetime decay curves recorded at three different locations on a defect.

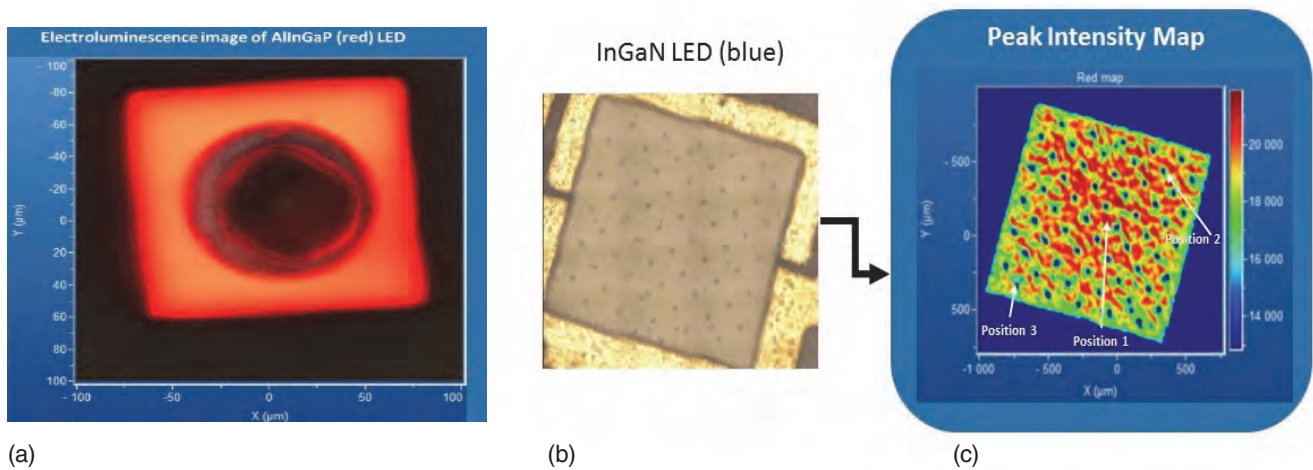


Figure 3 (a) Representative electroluminescence image of AlInGaP LED and (b) Optical micrograph and (c) PL intensity map recorded from a InGaN LED. Defect region appeared as cold spots on PL map.

interested in the uniformity of the epitaxial deposition on a large wafer, so that a Lidar laser die cut from one part of the wafer can be expected to perform and behave as one from any other part of the wafer. Once again, this property is readily characterized using a photoluminescence (PL) intensity distribution across the wafer (Figures 2a and b). If, for some reason, some of the dies from this wafer do not show optimal luminescence compared to others, the process engineer might be interested in understanding the nature of the defects causing this sub-optimal luminescence efficiency (cold spots). Figure 2c shows a high resolution PL map of a defect. Sometimes, the charge carriers are captured at the defect sites and don't emit light.<sup>[2]</sup> Time-resolved PL sheds more light on defect properties.<sup>[3]</sup> Figure 2d shows PL lifetime decay curves from three locations close to a defect. At the defect center, significantly shorter lifetime was observed.

As part of a QA process, the engineer might want to measure the performance of the device under conditions similar to actual use by measuring the electroluminescence of the device before it is packaged (Figure 3a). PL mapping can also be used to analyze the final device as well. Figure 3 (b-c) shows results from an InGaN LED sample, where the PL map detected local luminescence variations.

### Example 2: Photovoltaics

Development and fabrication of Photovoltaics show a similar need for multimodal characterization. For example, at the material stage it is important that the material bandgap be engineered to optimally absorb the solar spectrum. Once again, PL is a good technique for determining that property (Figure 2a). The photovoltaic effect relies on the efficient movement of charge carriers either to the electrical load for use or to a battery for energy storage. Time-resolved PL is often used to characterize carrier dynamics (Figure 2d) or Raman spectra to

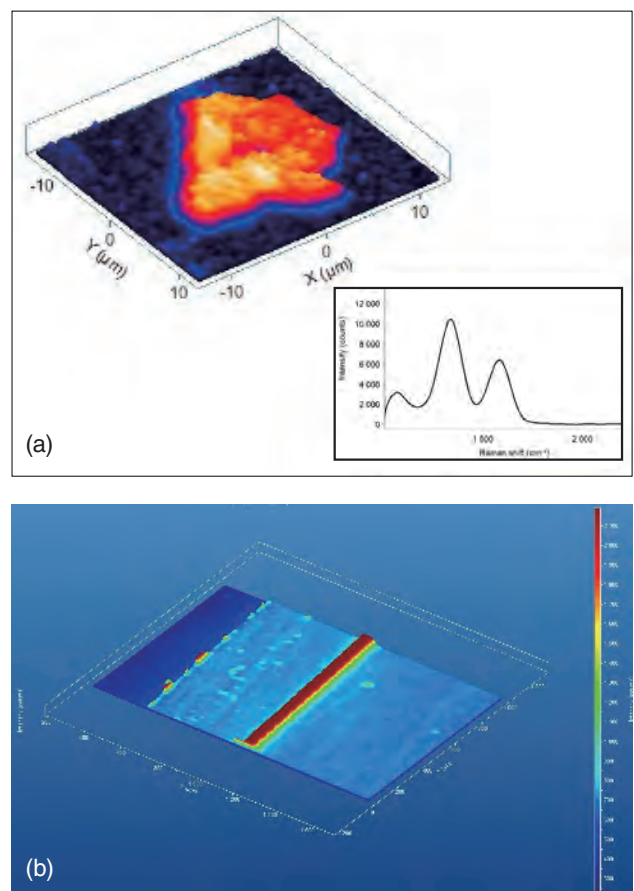


Figure 4 (a) Raman map and spectra (insert) of a possible contaminant flake on the surface of a semiconductor sample. (b) Photocurrent map of a sheet of Silicon PV material showing hot spots (possible defects). The red strip is a piece of the conducting electrode.

determine micro crystallinity (which in turn affects carrier dynamics (Figure 4a)). Finally, in the QA process of the solar cell device, one might be interested in measuring the overall device efficiency by measuring the spectral photocurrent response (Figure 4b).

Although contrived, the above measurements are typical occurrences in the design and manufacture of LED and



PV devices, and it is also common to see that all these measurements are typically made on different instruments. The novelty in this paper is showing that they can be made on one instrument (the SMS system from HORIBA), resulting in cost savings and adding convenience to the process.

### Correlative spectroscopy on semiconductor materials:

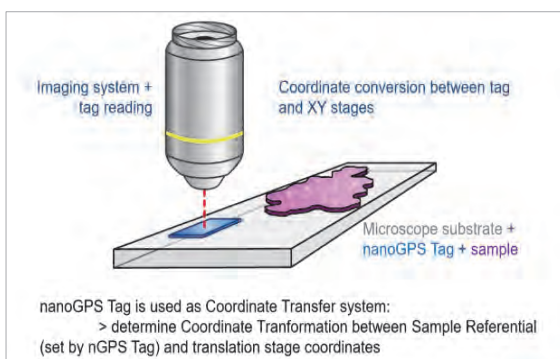
Simple, fast and non-contact microspectroscopy techniques such as the ones described above, are usually preferred in semiconductor material characterization, but it is sometimes necessary to use other, more complex, techniques that are not easy to combine with the above. For example, defect characterization sometimes requires high spatial resolution (nanometers) that is only available on instruments such as a scanning electron microscope (SEM) or an atomic force microscope (AFM). In those instances, and due to the cost and complexity involved in using a specialized instrument such as an SEM, it is desirable to establish a correlative optical spectroscopy so that such a defect can be identified in the future using a simpler spectroscopic technique, rather than doing the measurement on an SEM repeatedly, which can be costly and slow. To achieve this correlation, it becomes necessary to identify a nanoscale feature in the SEM, and to also be able to identify the same feature under an optical microspectrometer which can be laborious and time-con-

suming without some type of coordinate system matching between the two instruments. To facilitate this process, automated nanoscale coordinate transformation technologies, such as nanoGPS navYX™ from HORIBA have been developed to enable fast, accurate and repeatable localization of nanoscale objects between different measurement systems (Figure 5a). Figure 5c shows the cathodoluminescence map recorded from a Ga<sub>2</sub>O<sub>3</sub> nanostructure. Using nanoGPS, the sample was transferred to a HORIBA SMS system and a PL map was recorded successfully (Figure 5c).

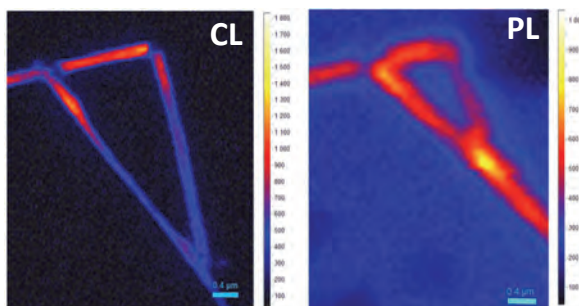
### Conclusion

In conclusion, speed, cost minimization and reproducibility are persistent drivers for decision making when it comes to instrumentation choices for semiconductor research and fabrication. In this paper, we introduce a novel modular and multimodal platform that enables the efficient combination of several complementary spectroscopic techniques relevant for semiconductor characterization on one platform. Furthermore, and for when it is necessary to measure across different platforms, we introduce a new coordinate transformation technology that enables the fast and accurate localization of nanoscale features across different measurement and metrology platforms. For further information about the different spectroscopies available on such a platform, please visit [www.microspectroscopy.com](http://www.microspectroscopy.com) and download the application handbook.

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(a)



(b)

(c)

Figure 5 (a) Schematic illustration of nanoGPS tag attached to the sample facilitates seamless coordinate transfer between two analytical systems. (b) Correlative cathodoluminescence (CL) and (c) PL measurements performed on a Ga<sub>2</sub>O<sub>3</sub> nano structure.

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**Praveena MANIMUNDA, Ph. D.**

Applications Scientist II  
Optical Spectroscopy Division (OSD)  
HORIBA Scientific



**Francis NDI, Ph. D.**

Global Product Line Manager  
Optical Spectroscopy Division (OSD)  
HORIBA Scientific

## In Operando Characterization of Li Composite Battery Electrode by Ellipsometry and Raman Spectroscopy. The Case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Based Anode.

Valerie SILLER

Alex MORATA

Juan Carlos Gonzalez-ROSILLO

Marc Nuñez EROLES

Michel STCHAKOVSKY

Albert TARANCON

Lithium titanium oxide thin films are increasingly popular anode materials for applications in lithium-ion microbatteries and hybrid supercapacitors, due to their improved safety, cost and cycle lifetime. Nanoengineering of their stoichiometry and crystallinity can modify their lithium-site occupancy and stretch the materials specific capacity. So far, research efforts have mainly focused on the pure spinel phase  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) and only a small fraction is dedicated to a broader spectrum of titanium-based metal oxide thin films. In this work, Pulsed Laser Deposition (PLD) is used by alternating LTO and  $\text{Li}_2\text{O}$  ablations to create a wide landscape in the composition of titania-based micro-anodes. Their structures are studied by Raman Spectroscopy (RS) and their performances by In Operando Spectroscopic Ellipsometry (SE).

### Key words

microbatteries, lithium titanium oxide, pulsed laser deposition, spectroscopic ellipsometry, Raman spectroscopy



### Introduction

The expected growth in the number of sensor nodes and other Internet-of-Things devices in the next decade imposes the development of sustainable micro-power

sources, whose manufacturing should preferably be compatible with Silicon processing methods for economic reasons. Titania-based electrodes are one among other alternative to metal Li matching these conditions, the most studied one being the spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ . The insertion

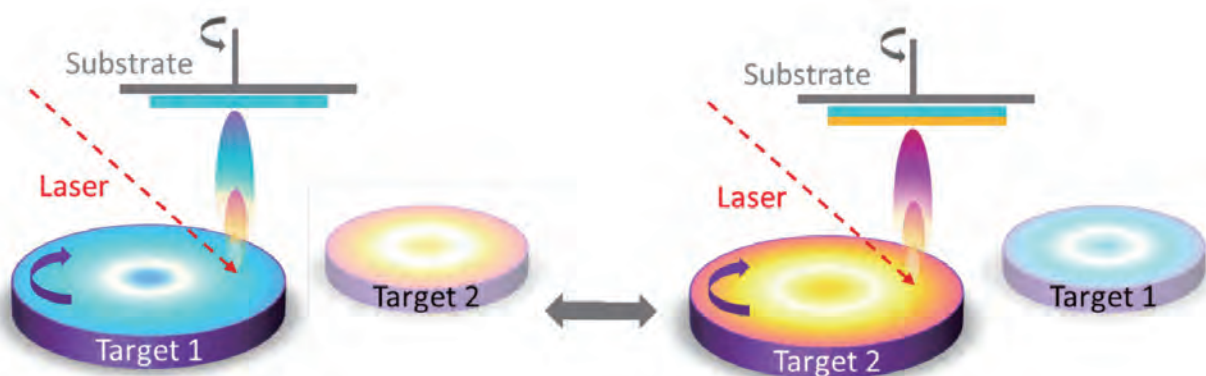


Figure 1 Multi-layer deposition in the PLD. A full cycle is completed after the ablation of each target with a fixed number of pulses. Two targets are alternated repeatedly in cycles until the desired film thickness are reached.

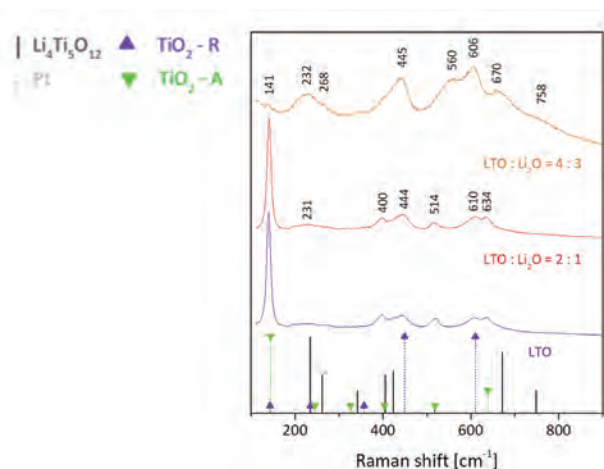


Figure 2 Raman spectra of LTO thin films with different amounts of additional  $\text{Li}_2\text{O}$ . Growth conditions are indicated with the deposition pulse ratio LTO :  $\text{Li}_2\text{O}$ . Raman references for  $\text{TiO}_2$  Rutile and Anatase are from literature.<sup>[1]</sup>

of extra lithium into the LTO structure would have a large impact on the accessible capacity of the battery assuming every  $\text{Ti}^{4+}$  is reduced to  $\text{Ti}^{3+}$ . Typically, LTO is used in the 1.5-3 V range because discharging to 0 V was reported to be unfavorable for the Li-ion diffusion beyond  $\text{Li}_7\text{Ti}_5\text{O}_{12}$ . Deeper insight about the structural consequences of cycling such alloys to very low potentials is one target of this work.

### Thin film fabrication

The concept of the multi-layer PLD deposition with two different alternating targets is schematically shown in Figure 1.

In this work, the targets were  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_2\text{O}$ . Depositions have been carried out on  $1\text{cm}^2$  Si wafer previously covered with Pt layer to provide electrical accessibility of the anode thin films.

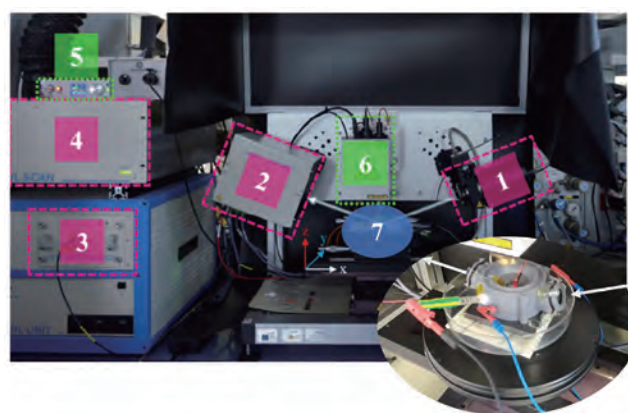


Figure 3 UVISEL (red) and Raman Superhead (green): 1: Polarizer, 2: Modulator, 3: Source, 4: Detector, 5: Laser, 6: Raman optics, 7 and insight: electrochemical cell for in operando studies.

### Analyzing tools, HORIBA Raman SuperHead and UVISEL Spectroscopic Ellipsometer

Raman spectra were collected using a HORIBA Raman SuperHead, coupled to an iHR320 monochromator equipped with a Sincerity CCD detector and a laser at  $\lambda = 532\text{ nm}$ .

Figure 2 illustrates the Raman spectra of structural evolutions of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  spinel phase upon a staggered lithium addition. It reveals the main presence of anatase and rutile phases and no evidence of spinel LTO for lower lithium contents. With increasing the  $\text{Li}_2\text{O}$  addition, the anatase signal vanishes and some vibrational modes of LTO become evident. Rutile appears to be present at any lithium concentration, which was confirmed by X-ray diffraction.

Literature has reported that nano-scaled  $\text{TiO}_2$  shapes have increased the capabilities of lithium uptake for titania-based anodes and promoted their electrochemical

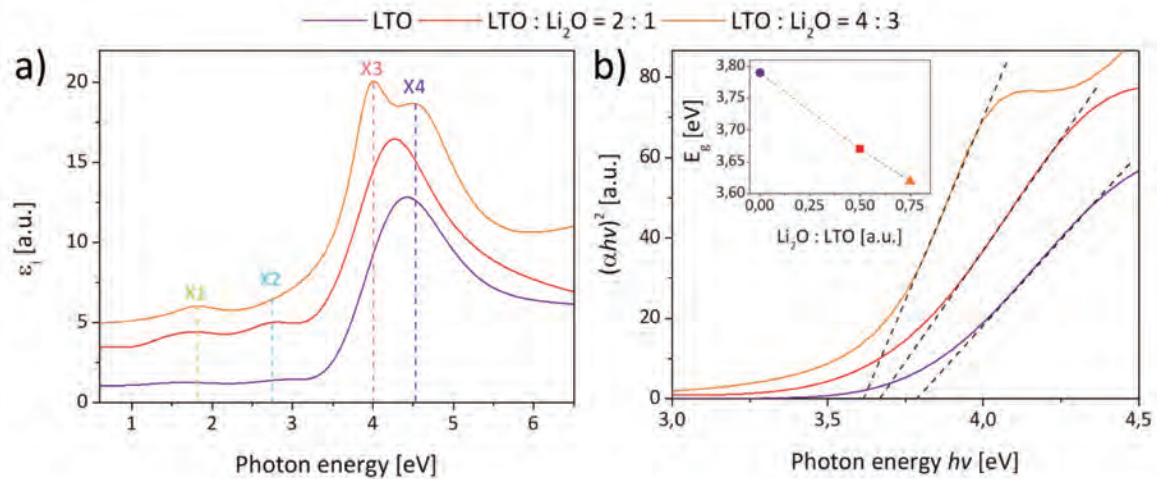


Figure 4 Imaginary part of the permittivity  $\varepsilon$  for LTO thin films for different LTO : Li<sub>2</sub>O ablation ratios in (a). Vertical dashed lines indicate significant changes in absorption bands upon lithium addition, marked and color-coded according to X1 – X4. In (b) the evolution of the band gap for different LTO : Li<sub>2</sub>O pulse ratio (as inset) are shown.

activity and performance in batteries<sup>[2-5]</sup>. While this report is being written, the scanning probe microscope for characterization of such nano objects in operando (HORIBA Electrochemical Tip Enhanced RS) is running first experiments at IREC.

UVISEL phase modulation ellipsometer by HORIBA Scientific was used for optical characterization of the samples. The setup, combined with Raman Superhead is illustrated on Figure 3.

While Raman informs on the structural properties, UV-Visible ellipsometry reveals thickness and optical properties of thin films, the latter correlated to their electrical properties. Figure 4 displays optical properties as imaginary part of dielectric function in a) and bandgap deduced from Tauc plot in b) for LTO with different Li concentrations.

Absorption bands (X1 – X4) occurring in Figure 4 (a) can be attributed to interactions between the electronic states of the Li<sub>2s</sub> orbital and the hybridized molecule orbitals of O<sub>2p</sub> and Ti<sub>3d</sub> forming the TiO<sub>6</sub> octahedra<sup>[6]</sup>. The evolution of these bands is highly correlated to Li diffusion modes through the film and can be controlled by in operando ellipsometry.

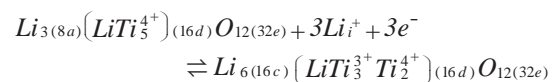
Let us first state that a detailed ex situ SE study of the optical properties of LTO:Li<sub>2</sub>O composites preceded the operando analysis. It allowed composition analysis by means of usual ellipsometric modeling of effective medium. Then, optical properties for layer evolution during cycling was compared to Figure 4, depending on the Li<sub>2</sub>O content and optical absorption bands could be assigned to specific Li ions energetic levels (and corresponding occupancy inside the spinel structure) according to literature. These results set a solid ground for further

SE analysis in a dynamic environment.

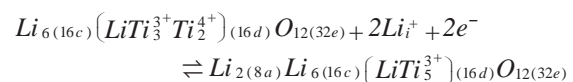
### Electrochemical performance of the films, discharge to very low potential

The electrochemical experiments have been achieved in 1 M LiPF<sub>6</sub> electrolyte and lithium acting as counter and reference electrode in a classic three-electrode setup.

From theory and literature<sup>[7,8]</sup>, the standard reaction potential for the intercalation of three Li<sup>+</sup> into spinel Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> is known to be 1.5 V vs. Li/Li<sup>+</sup> and follows a mechanism expressed in the following equation:



Under continued discharge below 0.6 V vs. Li/Li<sup>+</sup>, two additional lithium ions can be intercalated at tetrahedral 8a sites in Li<sub>7</sub>Ti<sub>5</sub>O<sub>12</sub> by reducing two remaining Ti<sup>4+</sup> as described in the different following equation:



Cyclic voltammograms (CV) and chronopotentiometry measurements have been collected at different current densities in the potential range of 0.3 – 3.5 V vs. Li/Li<sup>+</sup> and are shown in Figure 5 for different LTO : Li<sub>2</sub>O films. For the calculation of specific capacities, the thicknesses determined by SE have been implemented.

Constant current charge and discharge (chronopotentiometry) curves in Figure 5 (b, d, f) exhibit a steady increase in the specific capacities, strongly correlated to the addition of Li<sub>2</sub>O during deposition. Excellent charge/discharge profiles are reached with well-defined plateaus for the

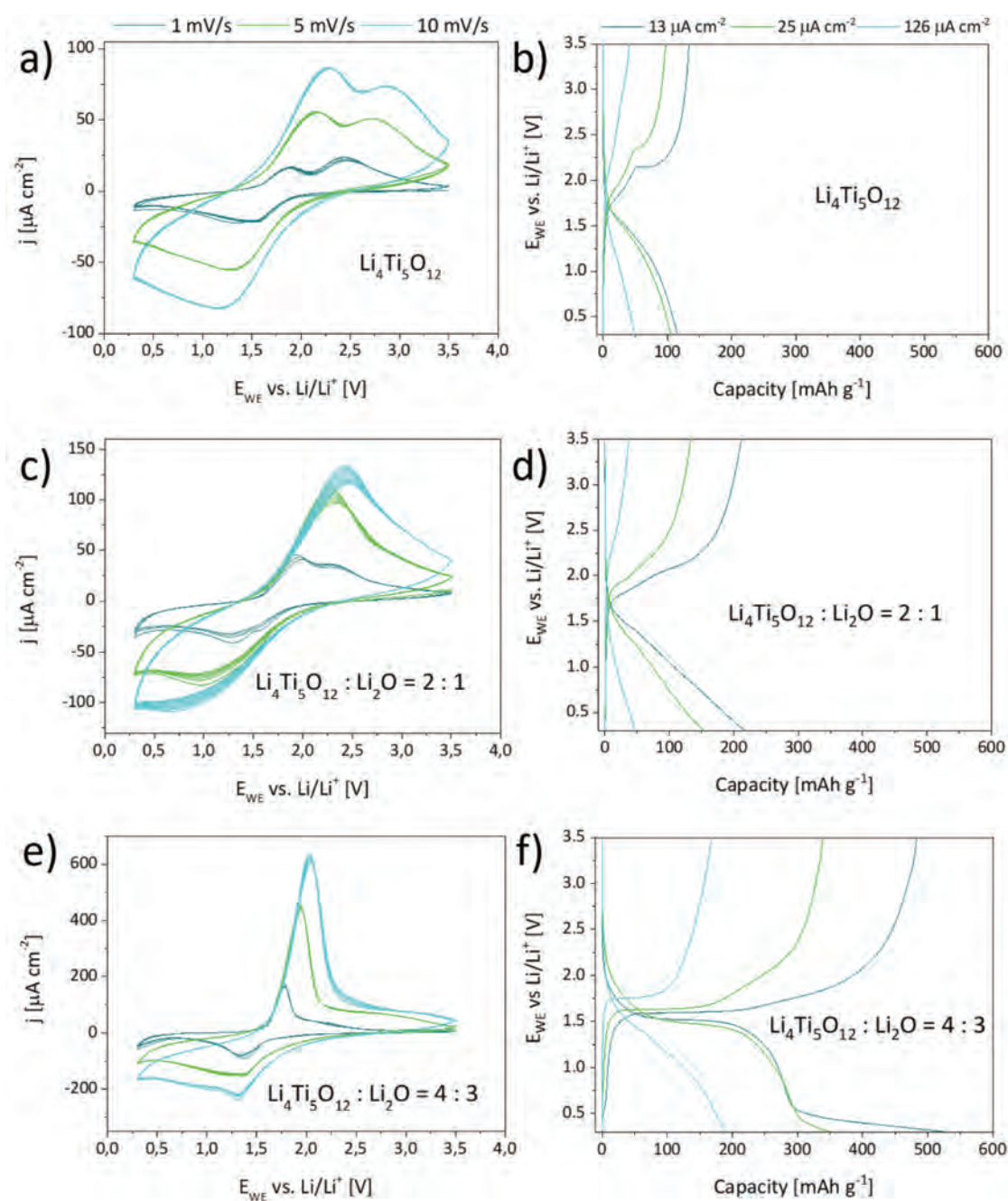


Figure 5 Cyclic voltammograms (left) and constant current charge/discharge curves (right) of LTO layers without additional  $\text{Li}_2\text{O}$  in (a,b) and with additional  $\text{Li}_2\text{O}$  in a pulse ratio of 2:1 (c,d) and 4:3 (e,f) for LTO :  $\text{Li}_2\text{O}$ , respectively. The electrochemical window ranges between 0.3 – 3.5 V vs.  $\text{Li}/\text{Li}^+$ . The applied current densities are  $13 \mu\text{A cm}^{-2}$ ,  $25 \mu\text{A cm}^{-2}$  and  $126 \mu\text{A cm}^{-2}$ .

$\text{Ti}^{3+/4+}$  transition (Figure 5 (f)) under further  $\text{Li}_2\text{O}$  addition, resulting in the extraordinary high specific discharge capacity of  $298 \text{ mAh g}^{-1}$  at 0.5 V vs.  $\text{Li}/\text{Li}^+$  for the 4:3 ablation ratio. An additional plateau appears to begin below 0.5 V vs.  $\text{Li}/\text{Li}^+$ , which may be attributed to the extra lithium uptake described earlier by Yi et al.<sup>[9]</sup> under the occupation of octahedral 16c and tetrahedral 8a sites.<sup>[10]</sup>

To obtain further insights about phenomena taking place at these very low potentials, we performed operando SE during the first cycle on a pristine film with high Li-content (LTO:  $\text{Li}_2\text{O}$  ratio of 4:3).

The first output of our SE analysis is the thickness evolution of the lithiated layer with time for the three different regimes (open symbols in Figure 6a referred to the right y-axis). Remarkably, the thickness evolution of the entire film follows quite accurately the shape of the charge injection for the 3 regimes, which indicates a change in volume upon lithiation/de-lithiation. In the imaginary part of the dielectric function, two distinctive features evolving with time are present in all cases, namely, a lower band at  $\sim 1.5 \text{ eV}$ , and a higher band at  $\sim 4 \text{ eV}$  (Figure 6b).

For regime I, our data are in excellent agreement with

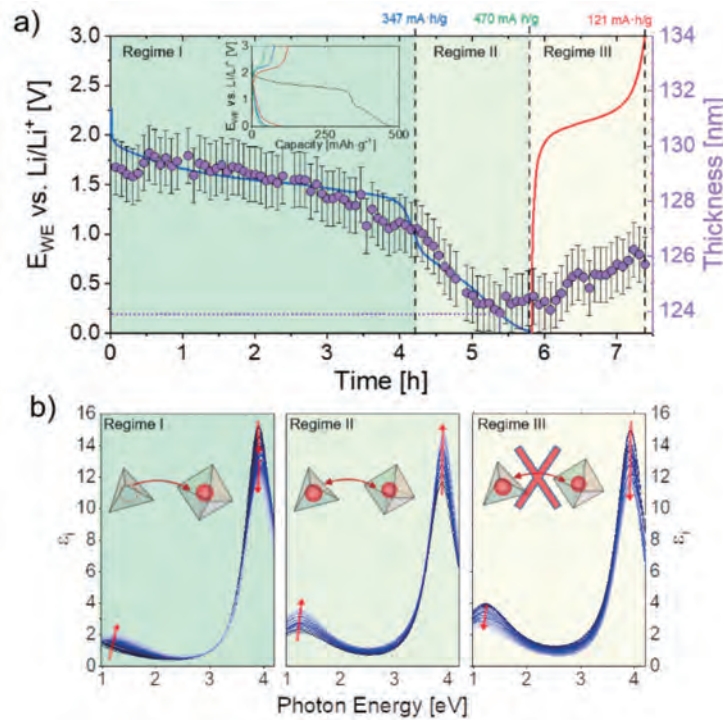


Figure 6 (a) Constant current charge and discharge curves collected under a current density of  $3.6 \mu\text{A cm}^{-2}$  (0.17 C-rate) monitored by operando SE. The inset shows the charge-discharge profiles of the operando experiment as a function of capacity. Right-axis (purple) shows the thickness evolution of the entire film with time. (b) Optical absorption as a function of the photon energy corresponding to the three different regimes described in the main text (arrows indicate the evolution with time along the experiment). Insets represent the lithium occupancy in the LTO lattice.

previous experimental results and first principle calculations predicting that during lithiation from  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  to  $\text{Li}_7\text{Ti}_5\text{O}_{12}$ , the intensity of the high energy band should decrease while the low energy band should increase<sup>[11,12]</sup>.

Beyond  $\text{Li}_7\text{Ti}_5\text{O}_{12}$ , i.e., regime II, the lithiation process is far less explored and, to the best of our knowledge, there is no experimental data to compare with. The increase in intensity of Dielectric function can be related to the role of oxygen in this regime upon further lithium insertions<sup>[13-18]</sup>

Finally, during the charging process (regime III), both energy modes decrease their intensity. In terms of Li occupation, these observations indicate that only the Li inserted in regime II (at the 8a tetrahedral sites) was extracted upon charging, while the Li inserted in regime I (at 16c positions) could not leave the structure.

Overall, our results back up the relevant idea that the cycling range of LTO-based systems can be safely extended until the limit of  $\sim 0.2$  V, which is beyond the typical value of 1V reported in the literature.

## Conclusion

In this work, Pulsed Laser Deposition (PLD) was used by alternating LTO and  $\text{Li}_2\text{O}$  ablations to create a widelandscape in the composition of titania-based

micro-anodes.

The alternating ablation of LTO and  $\text{Li}_2\text{O}$  targets in the PLD provides a good strategy to fabricate highly performing anodes. Stable cycling was achieved down to potentials of 0.2 V. The structural consequences of cycling in the low potential region during the first discharge were studied using in operando SE. These results provide guidelines to extend the useful cycling range of LTO-based anodes to increase their competitiveness versus Li-metal anodes.

## Note

This HORIBA readout contribution is a summarized version of the original paper “Safe extended-range cycling of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anodes for ultra-high capacity thin film batteries” published in *Materials Today Energy* 25 (2022) 10 0979.

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**Valerie SILLER, Ph. D.**

Catalonia Institute for Energy Research (IREC)



**Alex MORATA, Ph. D.**

Catalonia Institute for Energy Research (IREC)



**Juan Carlos Gonzalez-ROSILLO, Ph. D.**

Catalonia Institute for Energy Research (IREC)



**Marc Nuñez EROLES, Ph. D.**

Catalonia Institute for Energy Research (IREC)



**Michel STCHAKOVSKY, Ph. D.**

HORIBA Scientific,  
HORIBA FRANCE SAS



**Albert TARANCON, Ph. D.**

Catalonia Institute for Energy Research (IREC)



## High-resolution Piezoresponse Force Microscopy Imaging of a Few Layered 2D Ferroelectric

Ana I. PEREZ-JIMENEZ

Two-dimensional (2D) ferroelectrics are promising materials for future applications in advanced nanoelectronics. Piezoresponse force microscopy (PFM) is extensively used to investigate nanoscale-electromechanical properties. However, the underlying small mechanical deformations displayed by 2D ferroelectrics, ion conductivity, and side effects from tip-surface forces, complicate the high-resolution imaging of ferroelectric domains and domain walls in ambient conditions. Here, we demonstrate that the setup versatility of HORIBA AFM together with its scanning method “PFM-Top mode”, further improve signal sensitivity and spatial resolution when mapping low-dimensional ferroelectrics. This approach is demonstrated by the PFM imaging with up to 12 nm spatial resolution of ferroelectric domains, and domain walls, from a 16 nm thick  $\text{CuInP}_2\text{S}_6$  flake.



### Introduction

Ferroelectrics are crystals which structural lattice polarization can be reversed under an external electric field, and remain polarized even when the field is removed<sup>[1]</sup>. This quality of ferroelectrics has motivated the scientific interest for their potential application in developing future electronic, optoelectronic, and photovoltaic nanodevices<sup>[2,3]</sup>. However, the successful integration of classic ferroelectrics like thin-perovskites in nano-sized devices, remains

precluded by problems related to material degradation and ferroelectricity loss, when the thickness of the film shrinks to tens of nm<sup>[4,5]</sup>. In this respect, 2D van der Waals (vdW) ferroelectrics offer a means to overcome these downsides. Mainly, 2D-vdW ferroelectrics are nanometer-to-atomic scale thick, structurally stable, and prone to be controlled or modulated<sup>[5]</sup>.

Up to now, several 2D vdW ferroelectric structures have been theoretically predicted but a few experimentally

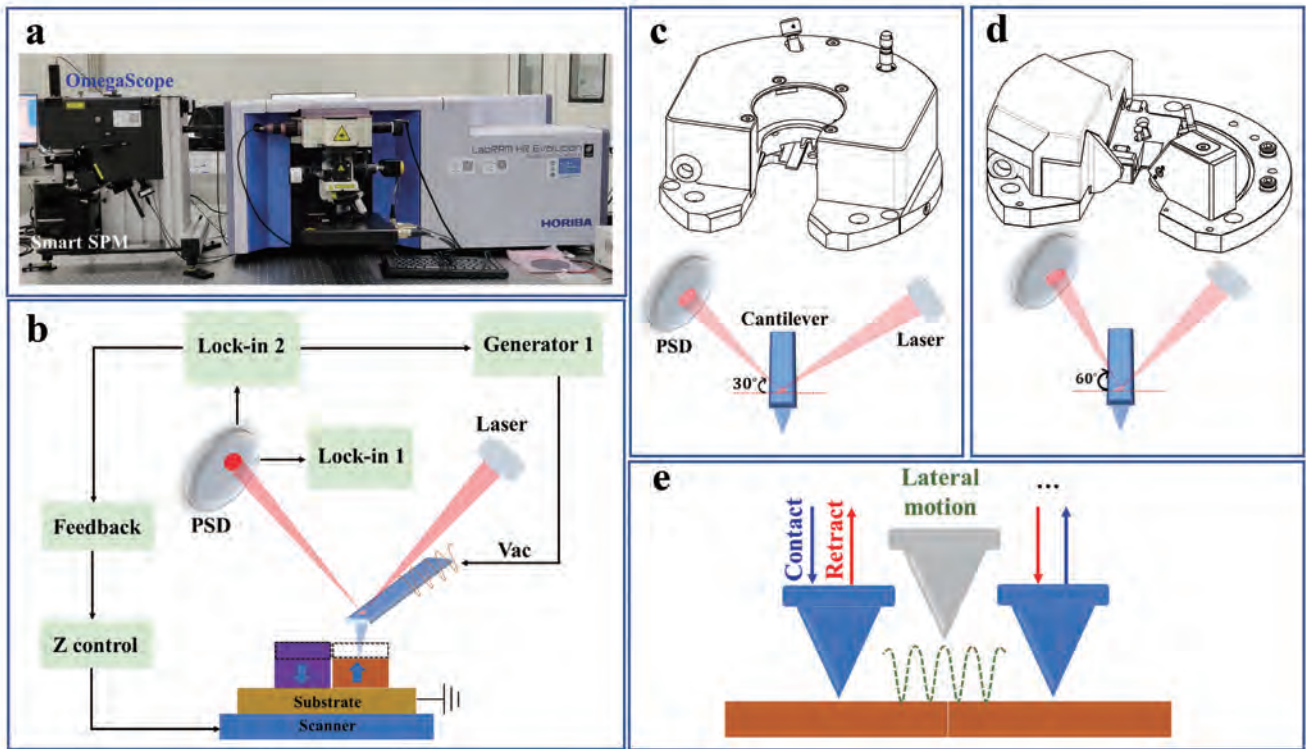


Figure 1 PFM operation principle and experimental set up in (a) HORIBA AFM-Raman. (b) Basics of PFM: a conductive tip is brought into contact with the piezoelectric sample. An alternating voltage (Vac) is applied to the tip at a given amplitude and frequency by the function generator (generator 1), while the sample substrate (or back electrode) is kept grounded. The generated oscillating electric field leads to the localized mechanical deformation of the sample (i.e., either extension or contraction). In turns, the resulting strain induces the deflection of the tip cantilever. The reflected laser signal is read out by a position sensitive detector (PSD) that is connected to two lock-in amplifiers. The output signals from lock-in 2 are the PFM amplitude and phase, which contain the information about the strength of the vertical electromechanical response, and the direction of the polarization, respectively. In addition, lock-in 2 is the main amplifier of the feedback-controller loop. While, the output readings from lock-in 1 are the lateral PFM amplitude and phase signals. Schematic drawing of AFM heads (c) HE002 and corresponding optical registration system; and (d) HE001 and its optical registration system. (e) Simplified sketch of the point-contact mode operation of PFM-Top mode.

proven<sup>[3,6]</sup>. To unequivocally verify ferroelectricity, the formation of well-defined ferroelectric domain patterns has to be observed<sup>[7]</sup>. Ferroelectric domains are nanometer-scale structures with opposite polarization and separated by boundaries known as domain walls. Nevertheless, it is challenging to observe nanoscale domains on materials with intrinsic small-vertical deformations and so, weak ferroelectric responses. This is even more critical when characterizing domain walls. Therefore, to further the experimental discovery, and application of 2D ferroelectrics for advanced nanoelectronics, the electromechanical properties of domain patterns, and domain walls have to be characterized with nanoscale-spatial resolution. PFM is conventionally employed to explore nanoscale electromechanical properties. Since the mechanical deformation (i.e., crystal lattice extension or contraction) induced by the applied electric field is recorded by means of the lock-in technique, strains in the order of picometres can be detected<sup>[1]</sup> (working principle in Figure 1b). Despite, when imaging piezoelectric responses at high-spatial resolutions, background noises considerably degrade the image signal-to-noise ratio (SNR). In addition, the tip-sample contact nature of PFM makes piezoresponse readings prone to artifacts generated by long-range electrostatic interactions. The use of stiff cantilevers (tens of N/m) helps to circumvent electrostatic-side

effects. Yet, at the cost of damaging either the tip or the sample. In this manner, the synergic effect of background noises and electrostatics interactions complicate the PFM imaging at high-spatial resolutions of 2D ferroelectrics.

Fortunately, HORIBA AFM offers practical solutions to these issues thanks to its versatile instrumental setup and scanning method PFM-Top mode (Figure 1). These advantages are explained and demonstrated below in the framework of working with HORIBA AFM-Raman (Figure 1a).

In the standard configuration of HORIBA AFM Raman, the Smart SPM (Figure 1a) is coupled to the AFM HE002 head (Figure 1c), which optical detection system is arranged such as the diode laser beam is reflected by the cantilever (at its rest position) to the PSD at an angle of 30°. The aim of this wide angle is to allow the top and side interface of the Smart SPM to the Omegascope (or Raman laser path, Figure 1a). Conversely, the reflected angle of the laser in the registration system of head HE001 is 60° (Figure 1d). With this narrower angle, the signal-collection efficiency (sensitivity) of the registration system is improved a tend fold compared to the sensitivity achieved with the wide angle: HE001's registration system noise <0.03nm vs HE002's registration system noise

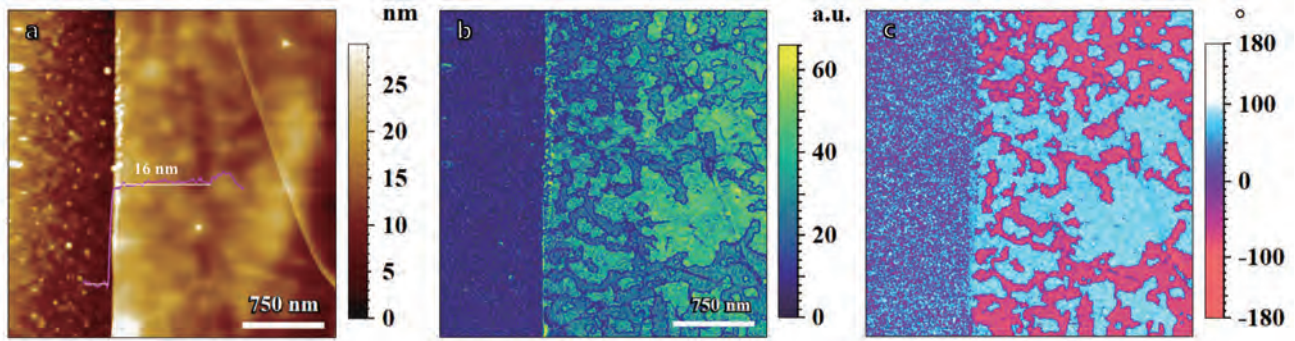


Figure 2 Topography and height-line profile (a), amplitude (b) and phase (c) images of a CIPS flake with a thickness of 16 nm. Experimental settings: driving PFM voltage ( $V_{ac}$ ) = 3 V; driving PFM frequency ( $f$ ) = 114 KHz (contact resonance); Probe = Pt/Ir coated Si tip, spring constant ( $k$ ) = 15 N/m; resolution = 256 x 256 pixels; humidity ~ 38%.

<0.1nm. The superior sensitivity performance of HE001 makes this head suitable to conduct AFM and/or NanoRaman experiments in liquid media. Notably, users can take advantage of this detection scheme to achieve ambient experiments in which resolving very short cantilever deflections is a must. This is the case of high-resolution PFM studies of ultra-thin ferroelectric materials. Because unlike to most of the AFM methods in which the lateral resolution depends on the tip radius, in PFM, this merit is strongly influenced by the material's elasticity<sup>[1]</sup>.

On the other hand, when scanning via PFM-top mode, the piezoresponse signal is recorded when the tip is in contact with the sample, while the lateral motion of the tip to the next measuring point is performed in semicontact mode (Figure 1e). This operation is repeated on each pixel of the image. The key advantages of this point-contact operation compared to plane-contact mode are the reduction of the tip-sample contact time (in the order of milliseconds) and lateral forces. In turn, short contact times minimize tip and sample damage, loading force drifts and indirectly, electrostatics side effects because stiff cantilevers can safely be used. On the other hand, abrasive lateral forces are avoided because the lateral motion between measuring points is performed in semicontact mode. The absence of lateral forces allows to resolve more precisely the fine contours of the objects.

Explained the instrumental and scanning advantages, in the following sections we probe the capabilities of HORIBA AFM for the high-resolution PFM imaging on ambient conditions of the 2D ferroelectric  $\text{CuInP}_2\text{S}_6$  (CIPS). CIPS is a vdW ferroelectric with unique properties such as negative piezoelectricity, negative capacitance behavior, and interchange between ferroelectricity and ionic conductivity<sup>[8]</sup>. Yet, its reliable nanoscale imaging for fundamental research is scarce due to complications from low ferroelectric signals and ion conductivity effect (see below).

## Piezoresponse imaging of a few layered CIPS

This section describes the PFM imaging of a 16 nm thick CIPS flake obtained by coupling the HE002 head to Smart SPM, and by the scanning method PFM-Top mode. The ambient topography, amplitude, and phase PFM images acquired simultaneously during scanning are shown in Figure 2a-c. The experimental conditions are described in the image's caption. The amplitude image (Figure 2b) reveals the existence of domain patterns with labyrinthine-like topology and uniform piezoresponse, but enclosed by domain walls exhibiting low signal strength (Figure 2b, dark-blue stripes). The phase image (Figure 2c) unveils a contrast between domains close to 180°, as expected for domains with opposite polarization. The formation of opposite polarized domain structures is direct evidence of material ferroelectricity and reliable PFM imaging. Notice that the PFM images depict clear signal contrast between domains and domain walls. However, a closer inspection of domain walls requires of higher spatially resolved images.

The PFM amplitude images obtained at different scanning areas are illustrated in Figure 3. At 3  $\mu\text{m}^2$  image size, the amplitude map depicts good SNR (Figure 3a) and consistent signal. At 2  $\mu\text{m}^2$  scan area (Figure 3b), the domain walls are well discerned, but the SNR is relatively lower compared to the amplitude map in Figure 3a. A further zoom of the scan area (Figure 3c) lead to the overwhelming of the piezoresponse signal by background noises. Such a poor PFM contrast precludes a robust evaluation of the lateral resolution, since background noises may broaden the width of the domain walls<sup>[1]</sup>. A tentative solution to improve the SNR is to increase the driving voltage ( $V_{ac} > 3\text{V}$ ). But this strategy is not recommended for CIPS since the polar structure and ferroelectricity can be severely damaged due to its high ionic conductivity<sup>[9,10]</sup>. Besides, high voltages can damage the thin structure of the flake. Thus, to avoid sample damage and the alteration of the ferroelectric properties, we concluded that the sensitivity

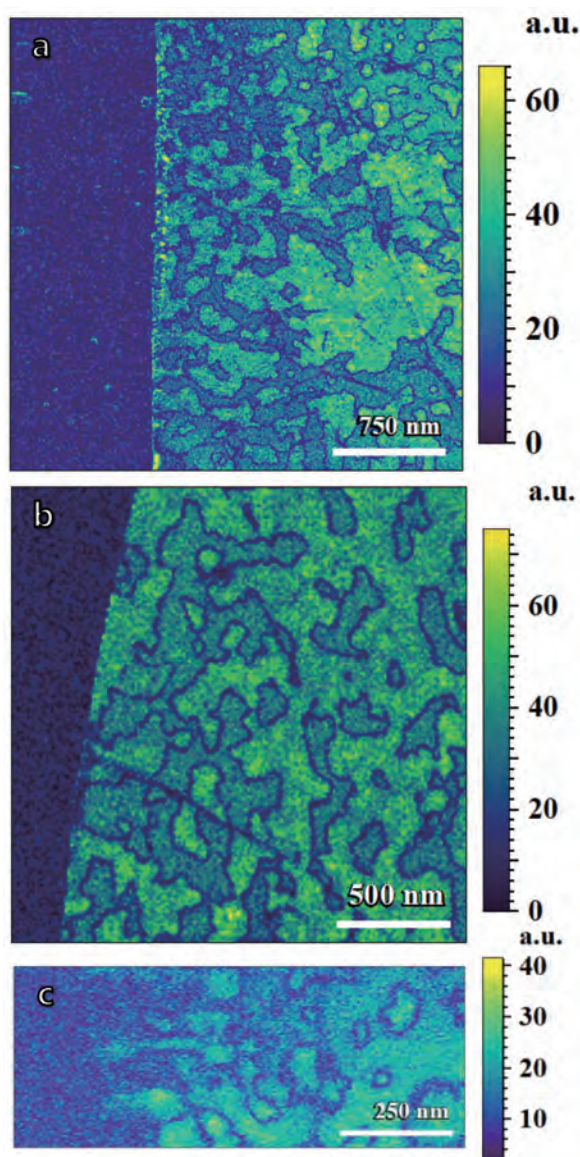


Figure 3 PFM amplitude images taken at  $3 \times 3 \mu\text{m}$  (a);  $2 \times 2 \mu\text{m}$  (b); and  $1 \times 0.4 \mu\text{m}$  (c) scan areas from a 16 nm-thick CIPS flake. Experimental settings:  $V_{\text{ac}} = 3 \text{ V}$ ;  $f = 114 \text{ KHz}$  (contact resonance); Probe = Pt/Ir coated Si tip,  $k = 15 \text{ N/m}$ ; resolution =  $256 \times 256$  pixels; humidity  $\sim 38\%$ .

of the present approach was not well-suited for the high-resolution imaging of the sample.

### Characterization of domain walls

To improve the image SNR and provide a most robust estimation of the achieved lateral resolution, the Smart SPM was coupled to the HE001 head. PFM Top mode was kept as the scanning method. Figure 4 shows the topography, amplitude, and phase high-resolved images ( $0.5 \times 0.5 \mu\text{m}$ ) acquired from the same 16-nm thick CIPS flake. Notice that the PFM maps (Figure 4b, c) exhibit greater SNR compared to those recorded with the HE002 configuration, although a lower driving voltage ( $V_{\text{ac}} = 2 \text{ V}$ ) was applied. Similarly, the domain patterns present clear  $180^\circ$  polarization contrast.

It is customary to estimate the PFM-lateral resolution by mathematically modelling the amplitude signal of a  $180^\circ$  domain boundary (Figure 4c, d). The resulting full width at half maximum (FWHM) is indicative of lateral spatial resolution<sup>[1]</sup>. Here, domain wall amplitude profiles from different locations were fit to the Lorentz function (Figure 4e). According to the estimations, the highest lateral resolution is about 12 nm, which corresponds to the measure of the domain wall profile 2 (Figure 4e). It is important to clarify that the estimated lateral resolutions calculated from the domain wall profiles are not their actual width.

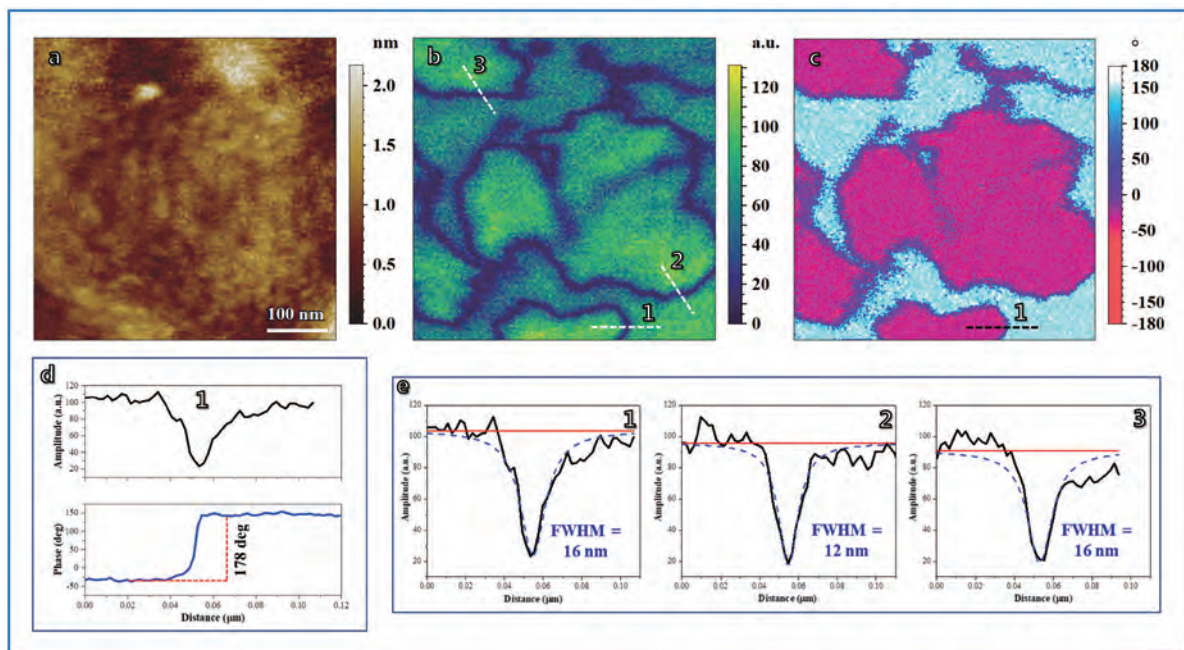


Figure 4 High-resolution AFM topography (a), amplitude (b), and phase (c) images of a 16 nm thick CIPS flake. Amplitude and phase profiles of a nearly  $180^\circ$  domain wall (d, black and blue dashed lines, respectively); domain walls amplitude profiles (e, black line) modeled by Lorentz function (e, blue dashed line). Experimental settings:  $V_{ac} = 2$  V;  $f = 114$  KHz (contact resonance); Probe = Pt/Ir coated Si tip,  $k = 15$  N/m; resolution =  $256 \times 256$  pixels; image size =  $0.5 \times 0.5$   $\mu\text{m}$ ; humidity  $\sim 38\%$ .

## Conclusion

In this work we demonstrated the setup versatility of HORIBA AFM together with its scanning method “PFM-Top mode”.

The combined use of the HE001 head and PFM-Top scanning mode permitted the high-resolution piezoresponse imaging in ambient conditions and low driving voltages of a few layered CIPS flake at 12 nm spatial resolution. The reliability of the measurements is supported by phase contrast values between domains close to  $180^\circ$ , and the topography integrity of the sample, even though cantilevers with several N/m were used. Hence, confirming non-destructive operation of PFM-Top mode.

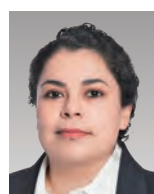
## Perspectives

Besides the characterization of ultrathin films and domain walls, the present strategy could be implemented to the investigation, in either ambient or liquid environments, of delicate and weakly piezoelectric materials like polymers and biological systems. Certainly, PFM imaging and fundamental studies will be greatly enriched when colocalized with optical techniques like normal and polarized Raman Microscopy, Second-Harmonic Generation (SHG), and NanoRaman. Definitely, correlative analysis will be ideal approaches to fully exploit the capabilities of HORIBA AFM Raman.

\* Editorial note: This content is based on HORIBA’s investigation at the year of issue unless otherwise stated.

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Ana I. PEREZ-JIMENEZ, Ph. D.

Senior Application Scientist  
HORIBA (China) Trading Co., Ltd

## Particle Size Studies for Biotechnology and Life Science

- Application Proposal from HORIBA Analytical Solution Plaza -

SHINOZAKI Yoko

SAIHARA Koji

mitsunari Kyoko

Particle size analyzers are used for R&D and quality control purposes in a wide range of fields, including ceramics, battery materials, catalysts, pigments, cosmetics, foods, and pharmaceuticals. In various industrial processes, the size of particles, including powders, is an important factor in characterizing the functionality of products. The application of particle size analyzers has been remarkably expanding not only in the field of nanotechnology, but also in the fields of biotechnology and life sciences. Particularly in the process of drug development and manufacturing, drug modalities are diversifying, including antibody drugs, nucleic acid drugs, cellular drugs, and gene therapy, as well as small molecule drugs, which have been the mainstream in the past and there is a growing need to evaluate cell-derived products such as exosomes, liposomes and drug delivery systems (DDS). Biopharmaceuticals have more complex molecular structures and must be analyzed and evaluated while considering the degree of damage to the sample. Therefore, conventional analytical principles and methods may not be applicable and different analytical approaches need to be considered. For small molecule pharmaceuticals as well, there are increasing demands for evaluation using different scales, rapid testing methods, high throughput and it is essential to propose analyzers and applications that satisfy these demands.

The HORIBA Group possesses multiple particle size analysis technologies that are suited to different measurement targets and offers a wide range of solutions. This paper focuses on dynamic light scattering technology, which has been gathering attention in recent years among particle size analysis technologies and introduces its applications in the fields of biotechnology and life science.

### Introduction

In the design of pharmaceutical products that affect the human body, various studies have been conducted to ensure efficacy and safety, to develop tablets that are easy to take, and to develop DDS (Drug Delivery System) that aims at more efficient drug delivery. Particle size is one of the most important design factors, and there are a wide variety of evaluation methods. To evaluate micron-sized particles that are common as raw materials and excipients for low-molecular-weight drugs, a number of measurement methods have been developed to suit the supply format, such as wet measurement methods in which particles are dispersed in water or organic solvents, dry measurement methods in which granulated powders are measured as powders, and other methods in which spray samples are measured. Particle size analyzers for this size

range are commonly based on laser diffraction and scattering. On the other hand, for particle size evaluation of nano-sized particles such as polymers and biopharmaceuticals, instruments based on the dynamic light scattering principle are effective.

As shown in Figure 1, HORIBA offers various applications in the fields of biotechnology and life science. This

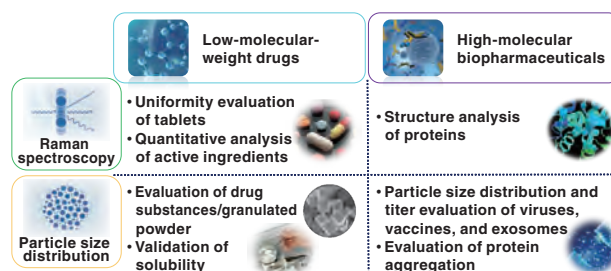


Figure 1 Analytical cases for small molecules and biopharmaceuticals.



Figure 2 Equipment nanoPartica SZ-100V2.

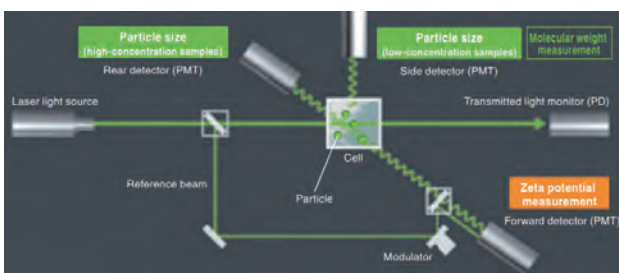
paper introduces examples of particle size distribution measurements for the biotechnology and life science fields, with a focus on products using particle size technology.

### Dynamic Light Scattering Technology

#### Dynamic Light Scattering (DLS)

Particles are in Brownian motion in the liquid phase and when these particles are irradiated by laser light, the laser light is scattered to various angles. By following the time variation of the scattered light intensity at a fixed point from a certain angle, we can observe the fluctuation of the scattered light intensity associated with the Brownian motion of the particles. Since small particles move fast and large particles move slow, the scattered light intensity fluctuates at a high frequency for small particles and at a low frequency for large particles. From the fluctuation signal of the scattered light intensity, an autocorrelation function is calculated, and the diffusion coefficient is calculated by processing the autocorrelation function. From the diffusion coefficient, the particle size can be determined using the Stokes-Einstein equation. This is the principle of DLS (Figure 3).

Analyzers using DLS can also measure zeta potential using the laser Doppler method and molecular weight from light scattering intensity using Debye plots.



Stokes-Einstein equation

$$d = \frac{k_B T}{3\pi\eta D}$$

$d$ : particle size,  $k_B$ : Boltzmann constant,  $T$ : absolute temperature,  $\eta$ : viscosity,  $D$ : diffusion coefficient

Figure 3 Optical system of nano partica SZ-100V2.



Figure 4 Gel unit.

Recently, there is also a gel unit option (Figure 4) that enables gel analysis. Similar to the fluctuation of scattered light due to the Brownian motion of particles, gels also have fluctuations in the scattered light. Because gels contain solvent in their mesh structure and their structure is fluctuating, the scattered light obtained by irradiation of laser light can have fluctuation information. In many cases, the mesh structure of a gel differs depending on the position, so a single point measurement in a homogeneous system, such as particle size, cannot represent the entire gel. Therefore, it is necessary to measure at multiple points and get the average.

#### Particle Tracking Analysis (PTA)

In PTA, a camera is used to observe the bright spots of particles in Brownian motion. Since the particle size distribution is obtained by counting particles one by one, the vertical axis is an absolute value, and the greatest feature of PTA is that it provides information on the number concentration of particles. The principle is to irradiate a laser beam onto particles in Brownian motion in the liquid phase, observe the light scattered by the particles on the CMOS camera screen, and track the movement of individual particles (Figure 6). The diffusion velocity is calculated from the distance traveled by the scattered light, and the diffusion velocity is converted to the particle diameter by the Stokes-Einstein equation, which enables the particle size distribution to be obtained. The number concentration can also be calculated from the number of



Figure 5 ViewSizer3000.

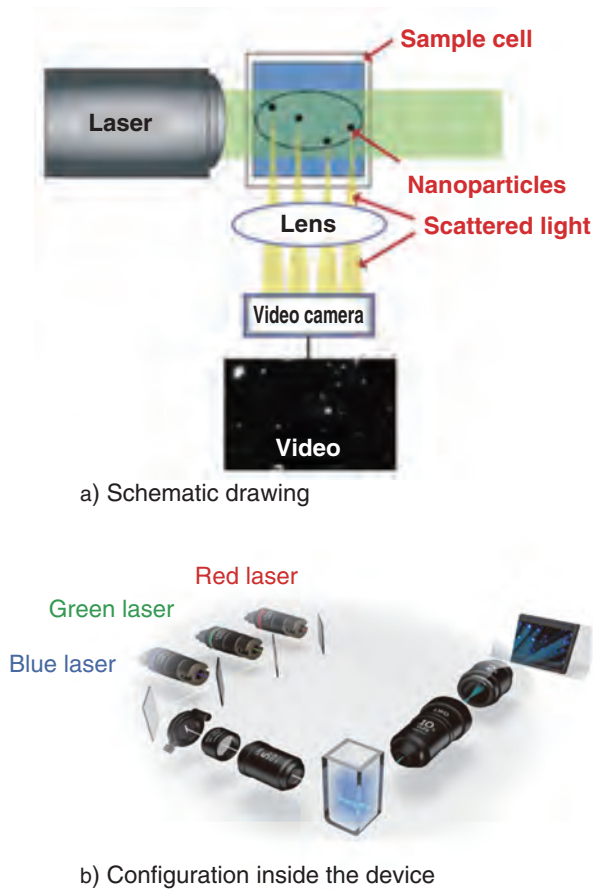


Figure 6 Instrument configuration of ViewSizer3000.

scattering centers captured on the camera screen and the volume of the measurement section. Furthermore, if particles have fluorescent characteristics, they can be separated from the scattered light using a fluorescent filter, allowing measurement of particles with fluorescent characteristics separately.

The PTA-based ViewSizer 3000 is equipped with a laser light source with three wavelengths, enabling simultaneous analysis of a wide range of particle sizes, from small to large, and it particularly suited to measure polydisperse samples. It is also possible to measure fluorescently labeled samples by using fluorescent materials that match the respective wavelengths. Furthermore, the sample cell design that includes periodic mixing of the sample ensures high reproducibility.

## Application Examples

### Example of exosome analysis

Exosomes are one of the extracellular vesicles ejected from cells. Exosomes contain functional factors such as membrane proteins and miRNAs derived from the ejected cells, and since exosomes can provide information on cell behavior, they are attracting attention in regenerative and preventive medicine, such as biomarker and drug efficacy research. Research is also being conducted to analyze the

functional factors expressed by exosomes, one of which is a technology for fluorescent labeling and discrimination of specific functional factors. PTA can discriminate particles with fluorescent characteristics and determine their number concentration and particle size distribution. In this paper, we will describe an example of fluorescent labeling of CD9, a membrane protein contained in exosomes, and evaluation of the number concentration and particle size distribution using PTA.

First, the size distribution and number concentration of all particles of exosomes derived from human serum were measured. Next, particles fluorescently labeled with Alexa 488 for CD9, a membrane protein of human serum-derived exosomes, were viewed on the camera screen, and particle diameter and particle number concentration were measured in the fluorescence measurement mode (fluorescence only was observed by using a long-pass filter (LPF) to cut off scattered light). The number concentration of total particles was  $2.3 \times 10^8$  counts/mL and that of fluorescent particles was  $5.5 \times 10^7$  counts/mL, indicating that approximately 24% of exosomes expressed CD9. (Figure 7 and Figure 8)

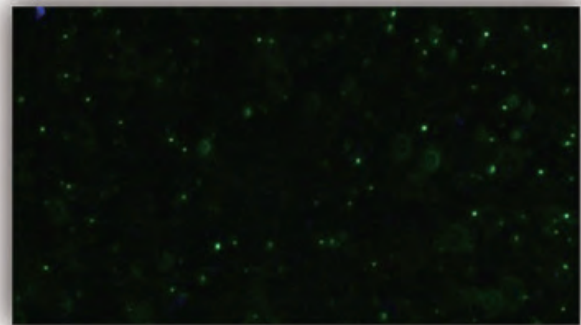


Figure 7 Exosome whole particle image by ViewSizer3000.

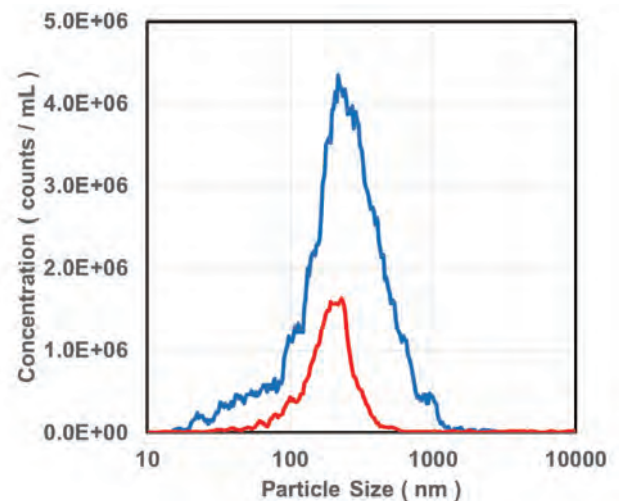


Figure 8 Comparison of ViewSizer3000 results between exosome whole particles and fluorescently labeled particles.  
 — : Exosome whole particles  
 — : Fluorescence labeled particles.



### Example of liposome analysis

Many factors that determine whether a drug treatment is successful or not remain unknown, partly because there is no way to confirm that the drug has reached the target tumor tissue. In recent years, research on drug delivery systems (DDS) has progressed, and a promising approach utilizing liposome has been developed. This innovation relies on the property of liposomes to form a closed lipid vesicle structure encapsulating an aqueous phase inside the lipid bilayer membrane. Many “liposomal drugs” are already on the market. On the other hand, focusing on the lipid bilayer, which is a component of liposomes, it is possible to reconstitute proteins, etc. in the lipid bilayer and therefore, it is thought that the use of photosensitizers, etc. will make it possible to confirm that the target tumor tissue is reached. Therefore, liposomes are expected to be a useful tool as “theranostics” that has both therapeutic (Therapy) and diagnostic (Diagnostics) functions (Figure 9). In DDS, the particle size of liposomes should be designed to be 20 to 200 nm, taking into account the EPR effect\* in tumors (Figure 10).

In this paper, we present a case study of liposomes as a theranostics formulation, in which we investigated the effect of photosensitizer content in the lipid bilayer on the particle size of the liposomes.

Liposomes were loaded with photosensitizers in various proportions and the particle diameters of the liposomes at various content levels (0.0, 0.5, 1.0, 5.0, and 10.0%) were measured using a dynamic light scattering analyzer nanoPartica SZ-100V2. The results showed that the particle size distribution of liposomes (Figure 11) became broad and the arithmetic mean diameter increased with increasing photosensitizer content. In both cases, the EPR effect was confirmed to be within the range of the EPR effect.

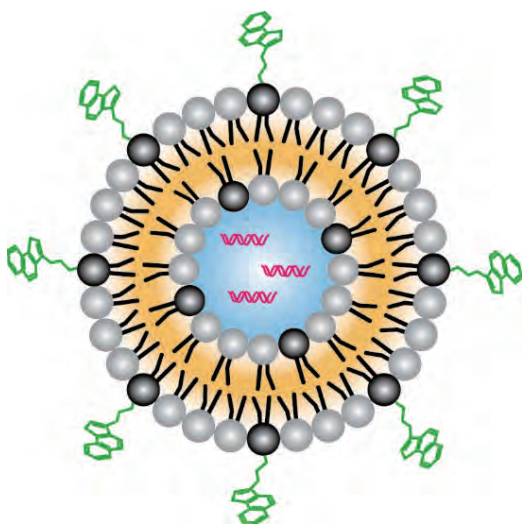


Figure 9 Theranostics Liposomes.

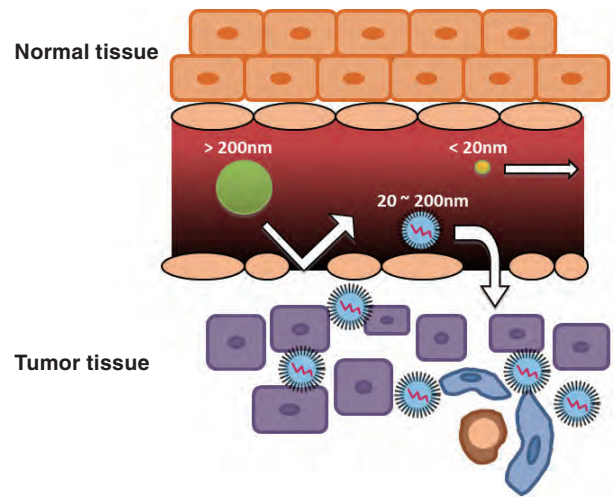


Figure 10 EPR effect.

\* EPR effect: The vascular endothelium of tumor tissue has a coarser crevice structure than that of normal tissue, which allows particles of a specific size (20-200 nm) to penetrate more easily.

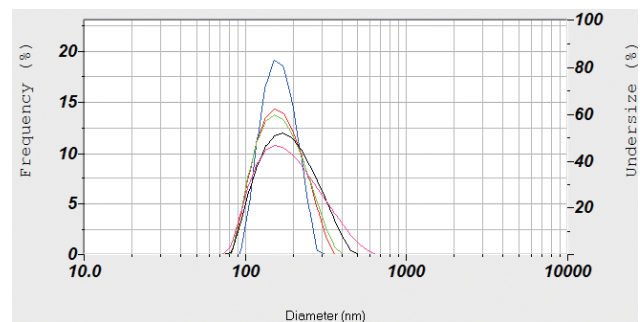


Figure 11 Particle size distribution depending on surface drug content. — : 0.0% — : 0.5% — : 1.0% — : 5.0% — : 10.0%

The dynamic light scattering measurements provide insight into the “photosensitizer content that reconstitutes the lipid bilayer” and the “particle size of liposomes” (related to the EPR effect). Combining these results with those obtained from zeta potential and fluorescence measurements, we can more accurately evaluate the diagnostic function of liposomes as theranostics.

### Example of Analysis of Cellulose Nanofiber

Cellulose nanofiber (CNF) is a fibrous material made mainly from cellulose obtained from biomass such as wood and pulp, and has many characteristics such as lightness, high strength, high transparency, high elastic modulus, low linear thermal expansion coefficient, and large specific surface area. Because of its low environmental impact, its use has been studied in various fields, including automobiles, home appliances, housing and building materials, cosmetics, and life sciences and its

practical application is also progressing. CNF is classified as a physical gel, and is physically entangled, and the entangling force includes not only three-dimensional entanglement but also electrostatic force. The mesh structure collapses when force is applied. Therefore, at present, only rheological and other evaluations are available, and the analysis of mesh structure using nanoPartica SZ-100V2 gel units, which can be evaluated in terms of distribution and numerical values, is attracting attention. As mentioned above, gels have a non-uniform mesh structure from place to place, so it is necessary to change the measurement points and average the results. The gel unit, developed as an option for the Dynamic Light Scattering Particle Size Distribution Analyzer, automatically operates the measuring cell in the vertical direction, enabling measurement at multiple points.

The following is an example of analysis of CNF with different cellulose concentrations using this gel unit.

Samples with cellulose concentrations of 0.2%, 0.5%, and 1.0% were measured (Figure 12). For each sample, the autocorrelation function was measured at 10 different measurement points of 100 μm each and the averaged results are shown in Figure 13. It was confirmed that the higher the cellulose concentration, the smaller the mesh size became.

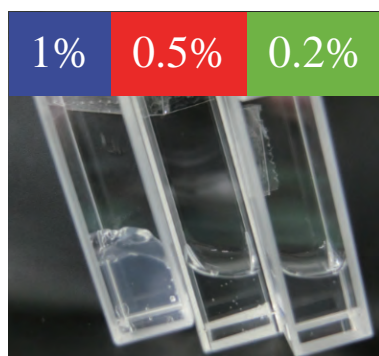


Figure 12 Samples with various cellulose concentrations.

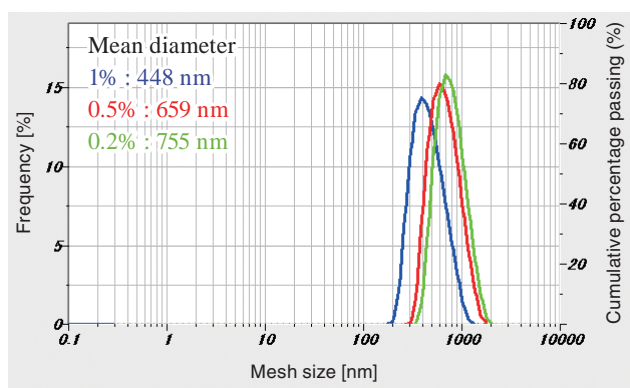


Figure 13 Mesh size distribution at various concentrations of CNF.

As described above, we expect to contribute to the fields of biotechnology and life science, including applications for exosomes, liposomes, and CNFs, and we intend to expand the scope of our efforts so that we can offer proposals for various modalities by utilizing the features of the various products in HORIBA’s product lineup. We look forward to expanding our efforts to offer solutions for various modalities by taking advantage of the features of HORIBA’s product lineup.

## Conclusion

In this paper, we focused on particle size distribution, especially dynamic light scattering in the biotechnology and life science fields, and introduced some examples of analysis along with their measurement systems. We have shown that dynamic light scattering can contribute from various angles, such as evaluation using a different scale, establishment of rapid testing methods, and high-throughput, by being used for analysis of various modalities as well as conventionally used low-molecular-weight pharmaceuticals.

In addition to dynamic light scattering technology, particle size distribution is also contributing to various research and development, such as the analysis of fluorescent bacteria using laser diffraction/scattering particle size technology. The HORIBA Group is constantly working to develop analytical measurement technology and to propose analytical methods. We will work together with our customers on the issues they face and strive to provide total solutions on which they can rely on our experience.

\* Editorial note: This content is based on HORIBA’s investigation at the year of issue unless otherwise stated.

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**SHINOZAKI Yoko**

Analytical & Testing Technology Department  
Analytical Technology Division  
HORIBA Techno Service Co., Ltd.



**SAIHARA Koji**

Analytical & Testing Technology Department  
Analytical Technology Division  
HORIBA Techno Service Co., Ltd.



**MITSunARI Kyoko**

Analytical & Testing Technology Department  
Analytical Technology Division  
HORIBA Techno Service Co., Ltd.

## Introduction of Non-destructive Elemental Analysis for In/Online Through Real Case Studies

AOYAMA Tomoki

UEDA Hideo

Automation and labor saving in the manufacturing process of industrial products have been adopted for the purpose of lower cost and higher quality. Inline analysis and online analysis are required actually to reduce labor costs and to perform full inspections, which used to be limited to sampling inspections. X-ray fluorescence analysis is a non-destructive and a non-contact method of elemental analysis, which was used mainly in laboratories. Now, it becomes to be applied to inline film thickness measurement in roll-to-roll processes, and on-line measurement of elements contained in oil, plating solution, wastewater, etc. In this report, examples of actual in-line and on-line measurements are presented.

### Introduction

X-ray fluorescence analysis is a common analytical technique used mainly in laboratories. The energy and intensity of the X-ray fluorescence emitted when a sample is irradiated with X-rays reveal the elements contained in the material and their composition ratios. There are two types of methods: the wavelength-dispersive method, in which the wavelength of the X-rays is separated by a spectrometer for measurement, and the energy-dispersive method, in which the energy of the X-rays is analyzed for measurement. HORIBA has been manufacturing and selling energy dispersive instruments since 1971 and has a lineup of : XGT series which converges X-rays and irradiates them to a small area to perform elemental analysis and measurement of elemental distribution in a small area; MESA series which irradiates X-rays over a wide area from the underside of a sample on a sample tray, enabling elemental analysis; and SLFA series which measures sulfur contained mainly in petroleum products. On the other hand, the analysis needs of the market are also changing with technological advances. In the analysis of industrial products, automation to save labor and 100% inspection to ensure high quality are desired due to increased cost and quality awareness, and such requests from customers are increasing. Since X-ray fluorescence analysis is non-destructive and non-contact, elemental analysis can be performed at a wide variety of sites as long as a small analysis module is available. In this paper, we will introduce a case study of the application of the MESA-50,<sup>[1]</sup> a compact X-ray fluorescence analyzer with a footprint of A4 size and an extremely compact X-ray

optical system. In-line and on-line automated analysis is applied to this optical system. The definition of in-line and on-line analysis in this paper is as follows. A conceptual diagram is shown in Figure 1.

**In-line analysis:** Direct analysis of a moving measurement object.

**On-line analysis:** The measurement object is diverged from the main flow and introduced into the analyzer.

### In-line analysis

In in-line analysis, a sample in the form of a sheet such as a film, a substance coated on a film, or a sample moving on a conveyor belt is continuously measured. The installation method must be individually designed to suit the production line. Of particular importance for this inline analysis is the time resolution of the measurement and the accuracy of the analysis.

Industrial products in sheet form are usually manufactured in a Roll-to-Roll process (Figure 2) and operates at very high speeds. The measurement time of a typical XRF measurement is tens to hundreds of seconds, so even if a measurement takes only a few tens of seconds, the sheet may move several tens of meters or more at the fastest, and the object to be controlled may be “hidden” from the analyzer. The measurement variation in X-ray analysis depends on the statistical variability of the X-ray generation (the total number of counts of X-rays obtained), assuming that the electronics of the instrument are stable.

Since the variation is inversely proportional to the square root of time, a trade-off with the measurement variation must be considered in order to shorten the measurement time. Although counts can be obtained by irradiating high intensity X-rays for a short time, the problem is that a large amount of X-rays saturates the detector, making it impossible to measure. To improve the saturation of the detector, the processing of the detector signal is speeded up. Normally, in energy-dispersive X-ray fluorescence analysis, the trapezoidal processing of signals (Figure 3) is performed with sufficient signal processing time per signal to ensure the energy resolution of the detector. This process causes a dead time during the measurement. By shortening the trapezoid processing time, the dead time is reduced and more signals can be received. This is an effective measure for in-line measurement where the energy resolution is poor because the target element is fixed, but the effect of interference with other elements is small. In addition to this, only the intensity of the required element is extracted to speed up the measurement.

Figure 4 plots the measured values of a stopped Ni foil of 2 μm thickness analyzed at 200 ms. The mean, standard deviation, and RSD of this measurement are shown in Table 1. Good results were shown for an XRF measurement with a very short time resolution.

Figure 5 shows the measurement results when samples with different thicknesses were operated. It can be seen that the thickness trend is obtained according to the difference in thickness. The shape of the measurement points per measurement can be calculated by the formula in Figure 6.

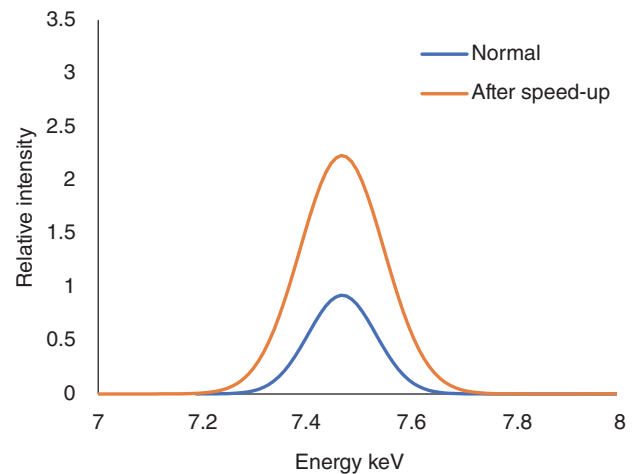
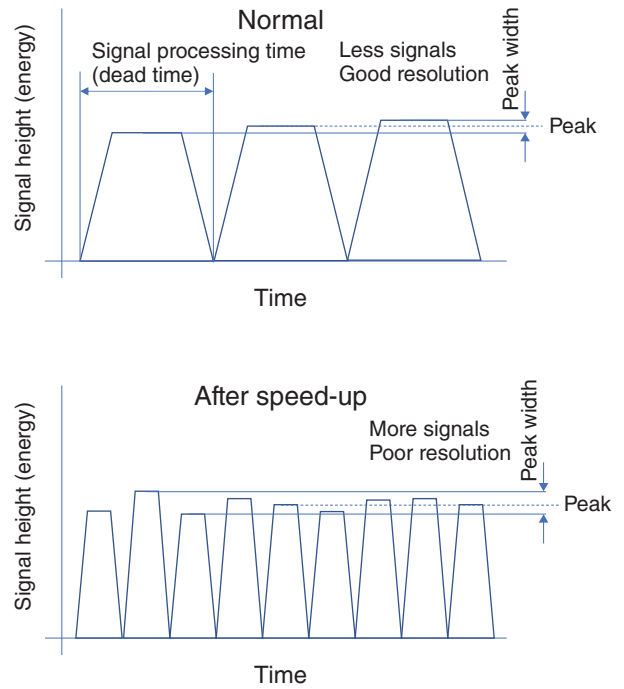


Figure 3 Signal processing.

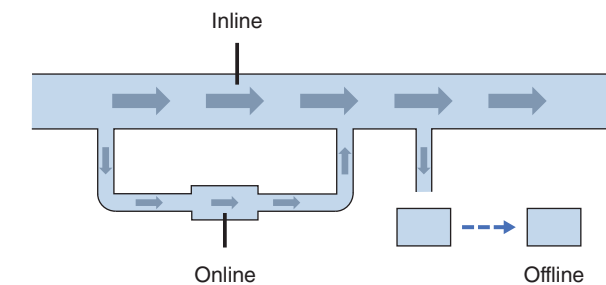


Figure 1 Conceptual diagram.

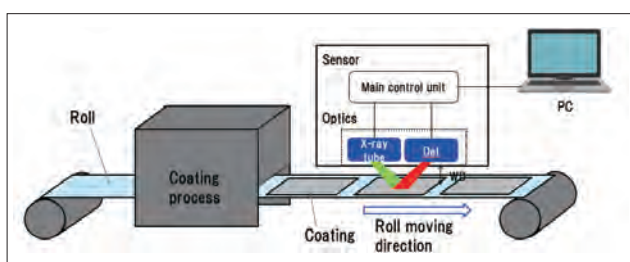


Figure 2 Roll to Roll process.

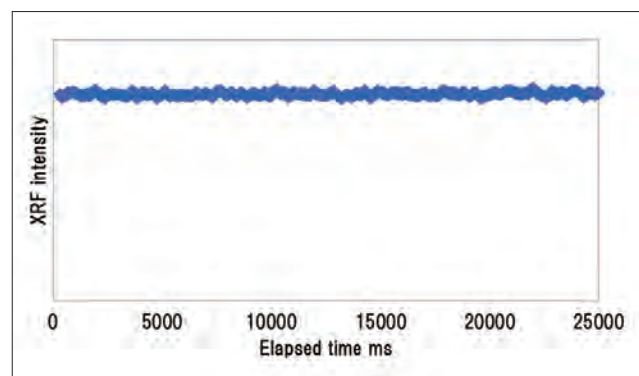


Figure 4 Result of 200 ms continuous measurement.

Table 1 Measurement results when the Roll is stopped.

Measured value μm	2.01
Standard deviation μm	0.02
RSD %	0.995

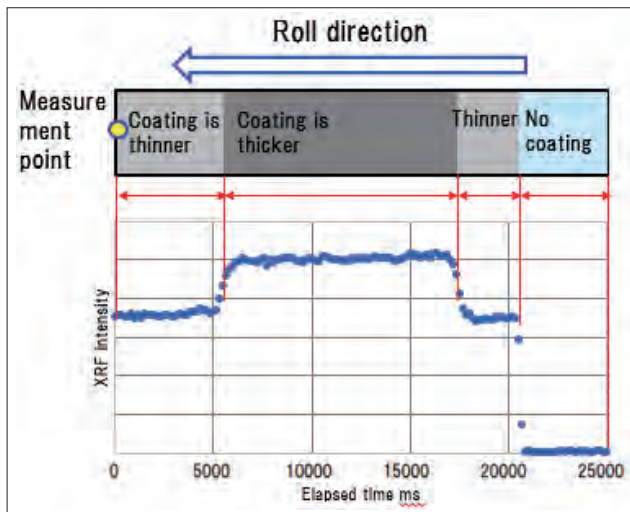


Figure 5 Measurement results during Roll operation.

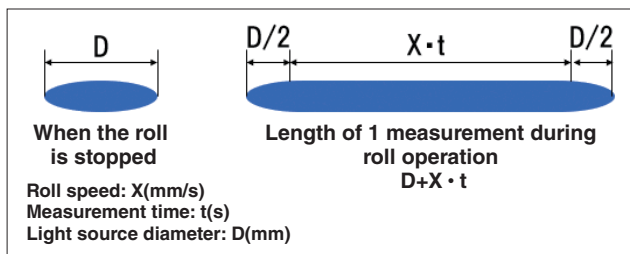


Figure 6 Shape of measurement point.

### On-line Analysis

In on-line analysis, continuous measurement (Figure 7) of a liquid sample supplied through piping to a flow cell set in an analyzer is performed. The structure of the flow cell (Figure 8) determines the performance of the analyzer, and although a thin resin film that easily transmits X-rays is often used for the X-ray irradiation section, a sturdy film with a certain thickness should be used in consideration of leakage of the liquid sample and deformation of the film during measurement. If the pumping pressure is high before branching, it is necessary to reduce the pressure before introducing the film into the cell in order to prevent damage to the film. When using a pressure reducing valve, cleaning should be taken to avoid

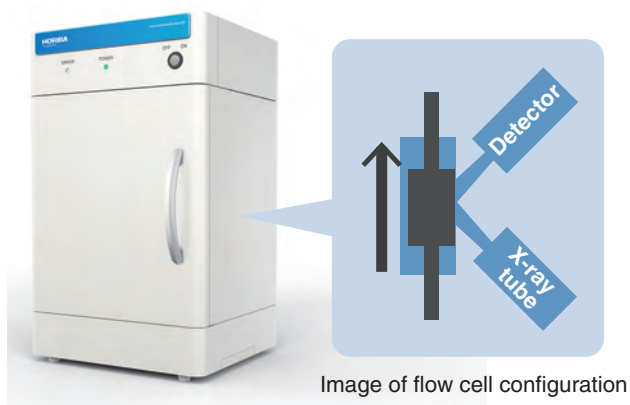


Figure 7 Flow example of MESA-50U.

clogging with solids.

When a highly viscous liquid sample is introduced, it may be heated to reduce the viscosity of the sample, and a sturdier film should be selected. A thicker film is more difficult for X-rays to pass through so there is a trade-off with analytical accuracy.

When measuring a liquid sample passing through a flow cell, if the sample adheres to the piping or the inner surface of the flow cell, the sample is measured by irradiating X-rays to a mixture of the residual liquid and the liquid that is currently passing through, and correct analysis values cannot be obtained. Therefore, it is desirable for the liquid sample to be replaced instantly. To achieve high replacement performance, it is necessary to eliminate protrusions in the piping and flow cell, and to use a material with good sliding properties for the inner walls. Figure 9 shows a graph of replacement performance when analyzing a heavy oil sample. It can be seen that the analysis values of the 0.2% sulfur and 1.0% sulfur samples switch within a few minutes.

If the replacement performance is not sufficient, a cleaning solution from another line is introduced to flush out the deposits on the piping and the inner wall of the flow cell. If the deposits are still not removed, or if a more accurate analysis is required, the piping and flow cell should be replaced with new ones.

If stable measurement is not possible due to deformation of the film caused by the flowing liquid sample, a valve can be installed after the branching to stop the flow to the flow cell (Figure 10). However, consideration must be taken to ensure that the replacement performance is not impaired by the retention of liquid sample by the valve.

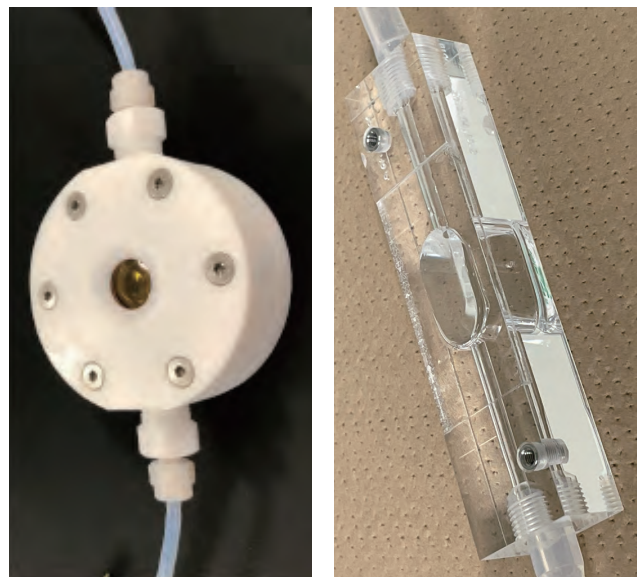


Figure 8 Example of flow cell.

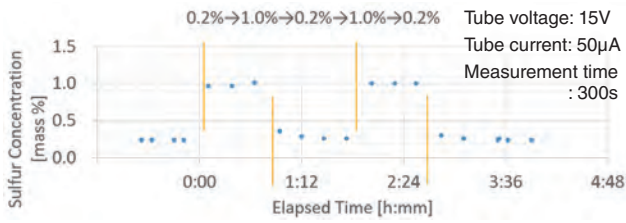


Figure 9 Replacement performance Data example (Heavy oil C).

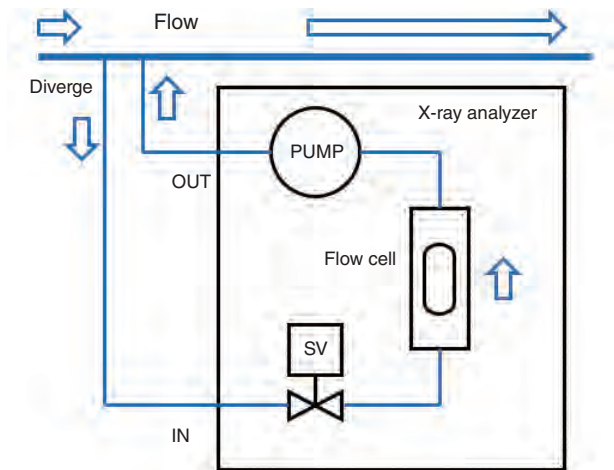


Figure 10 Flow example.

## Conclusion

As described above, in-line and on-line analysis enables the acquisition of a large amount of continuous data that would not be possible with human intervention. The large amount of data obtained enables early detection of abnormalities occurring in the process and trend management, which may lead to the discovery of events that could not be detected by laboratory analysis, in addition to automation and labor savings. We hope that the in-line on-line analyzers introduced in this paper will be widely used in various industrial product manufacturing sites.

\* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.

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**AOYAMA Tomoki**

Department Manager  
Scientific Instruments R&D Dept.  
Analytical Instruments (R&D) Research &  
Development Division  
HORIBA, Ltd.



**UEDA Hideo**

Scientific Instruments R&D Dept.  
Analytical Instruments (R&D) Research &  
Development Division  
HORIBA, Ltd.

# Facilities Introduction

## HORIBA Techno Service Introduce “Analytical Solution Plaza” HORIBA’s Services that Connect “Analysis” and “Understanding (Finding out)”

### SAKAGUCHI Mai

HORIBA Techno Service Analytical Solutions Plaza has areas for each of HORIBA’s focus markets such as “Energy & Environment”, “Advanced Materials & Semiconductors”, and “Biotechnology & Healthcare”. As a center connecting 18 application laboratories in Japan and overseas, HORIBA’s core analytical technologies are concentrated here.

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

### Analytical Solution Plaza Newly Established

HORIBA Techno Service, a group company of HORIBA, Ltd., takes charge of service business such as maintenance and inspection of HORIBA products. In recent years, in order to provide customers with even better solutions, we have been expanding our business from “selling products” to “selling services,” including product maintenance, contract analysis, user training, calibration, instrument testing and analyzer subscriptions.

In February 2021, as a project to commemorate the 20th anniversary of the establishment of HORIBA Techno Service, the Kyoto Head Office Building, the core base of our business, was constructed on a site adjacent to HORIBA, Ltd. Concurrently, we opened analytical application laboratories on the first and second floors and named it the “Analytical Solution Plaza.”

Measurement and analysis technologies are indispensable for the advancement of science and technology and the development of industry, and HORIBA wanted to have a place not only to disseminate technical information on analytical instruments, but also to listen to the opinions of customers in various fields and have interactive exchanges with them. With this in mind, the Analytical Solution Plaza aims to be a “place where HORIBA and our customers can interact” where people can gather freely, transcending the boundaries of technical fields. The laboratory area has been expanded to twice the size of the previous facility and analytical instruments has been set up in areas which HORIBA focuses on that are “Energy & Environment,” “Materials & Semiconductors,” and “Bio and Healthcare.”. The Analytical Solution Plaza is now a

hub connecting 18 analytical application laboratories in Japan and overseas, where core analytical technologies are concentrated.



Figure 1 HORIBA Techno Service head office building.



The logo (Figure 2) expresses its desire to be a place where various people and technologies are interwoven and to always transmit information to the world with a sense of speed. We aim to provide high value-added services as a solution partner to our customers.



Figure 2 Analytical Solution Plaza logo.

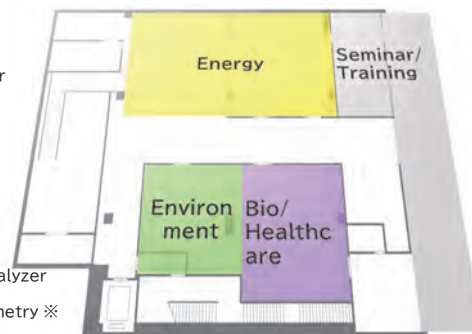


Figure 3 Analytical Solution Plaza floor.

**Energy**

- Carbon/Sulfur Analyzer
- Oxygen/Nitrogen/Hydrogen Analyzer
- Laser Scattering Particle Size Distribution Analyzer
- Nanoparticle Analyzer
- Centrifugal Nanoparticle Analyzer
- ICP Emission Spectrometer
- X-ray Fluorescence Sulfur-in-Oil Analyzer
- Gas Chromatography Mass Spectrometry ※
- Ion Chromatography※

**2nd Floor**



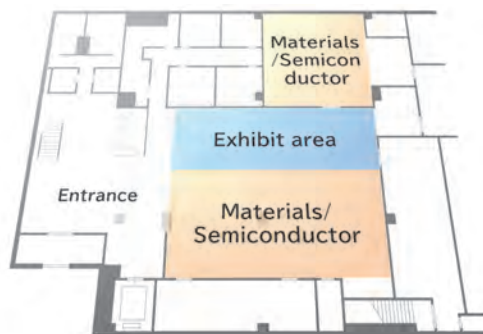
**Bio/Healthcare**

- Transmission Raman Spectrometer
- LC-Raman System
- Rapid Microorganism Detection System
- Molecular Interaction Analyzer (SPR)
- Fluorescence and Absorbance Spectrometer

**Environment**

- pH/water Quality Analyzer
- Oil Content Analyzer
- On-line TOC Analyzer
- Automatic Total Nitrogen/Phosphorus Monitoring
- Automatic COD Monitor
- Continuous Particulate Monitor with X-ray Fluorescence
- Portable Gas Analyzer

**1st Floor**



**Materials and Semiconductors**

- Laser Scattering Particle Size Distribution Analyzer
- Nanoparticle Analyzer
- X-ray Analytical Microscope (Micro-XRF)
- Fluorescence Spectrometer/Time Resolved Fluorescence Spectrometer
- Spectroscopic Ellipsometry
- Atomic Force Microscope Raman Spectrometer
- Confocal Raman Microscope
- Glow Discharge Optical Emission Spectrometry
- Scanning Electron Microscope※
- Field Emission-Scanning Electron Microscope※
- ※ Other companies' products

Figure 4 Analytical Solution Plaza equipment layout.

**Operating from around the world,  
We respond to all analytical and measurement needs**



Figure 5 HORIBA Group analytical application labs: 18 locations in Japan and overseas.

**Functions of Analytical Solution Plaza**

**Contract Analysis**

In addition to HORIBA products, the Analytical Solution Plaza is equipped with a variety of equipment such as sample preparation equipment, glove boxes and other sealed containers for samples that cannot be handled in the atmosphere and electron microscopes so that various analysis methods can be proposed. We can also modify our instruments and develop sample pretreatment equipment to meet your analytical needs.

**Analytical instrument use service**

We offer a new paid service for the use of analytical instruments at Analytical Solution Plaza (Kyoto and Tokyo), which can be used on a half-day or full-day basis. An analyst is present so that you can use the instruments while discussing directly with the analyst how to use them, the optimal measurement conditions and analysis methods. We also offer a subscription service in which you can rent analyzers for a fixed monthly fee.

**User Training**

The seminar room on the second floor is fully equipped with online studio facilities and other equipment, making it possible to conduct on-site analysis and online training from remote locations using remote functions. We also have training plans that utilize 3D data from MR (Mixed Reality) devices, and can respond to requests from both domestic and overseas customers.

**Calibration Service**

We calibrate equipment such as digital multimeters and balances 8nd issue traceability certificates. We also inspect PEMS (Portable Emission Gas Analyzer: device



Figure 6 Analysis scene.



Figure 7 Analytical instrument service.



Figure 8 Training.

name OBS) and gas dividers (GDC) used in road tests. As calibration services, we provide on-site JAB-accredited calibration services for MRA (Mutual Recognition Across the World) in the field of chassis dynamometers and emission gas measurement systems used in the automotive industry. Our accredited calibration certificates with the ILAC-MRA combined symbol are compliant with IATF 16949:2016, and our ISO/IEC 17025-compliant calibration certificates with the ILAC MRA accreditation symbol are also compliant with IATF 16949 requirements for automotive quality management systems.



Figure 9 Calibration service.

### Automotive Contract Testing

HORIBA offers various vehicle tests such as engine evaluation, catalyst test, fuel consumption test, etc., by combining measuring instruments including engine exhaust gas measurement systems, which are HORIBA's main products.

Our engineers with experience in engine development and vehicle inspection provide total support from bench testing to actual road testing. In recent years, we have also conducted tests on batteries and fuel cells installed in automobiles. In addition to power consumption tests and charge-discharge tests on battery modules and cells, we can also provide a full range of services from module processing and cell disassembly to evaluation of each material to enable various tests.



Figure 10 Automotive testing.

## Application Topics

### Analysis of cultural assets

#### I Kenji Miyazawa's Drafts: Cooperating to Determine Authenticity

We cooperated in analyzing the authenticity of a draft poem said to have been written by Kenji Miyazawa in the early Showa period.

This draft was investigated by Hanamaki City in Iwate Prefecture to determine if it could be an autograph, as it differed from previous drafts in that the red and black text were reversed and the signature of "Kenji" was missing. HORIBA Techno Service conducted elemental analysis of two drafts which were written around the same time, using a micro X-ray analyzer (XGT-9000). The determination of the type of elements contained in a material is one indicator of the type of ink, paper, and other materials used. Based on the results of this analysis and the results of previous research on Kenji Miyazawa, Hanamaki City announced that "this draft is an autograph draft of Miyazawa Kenji".

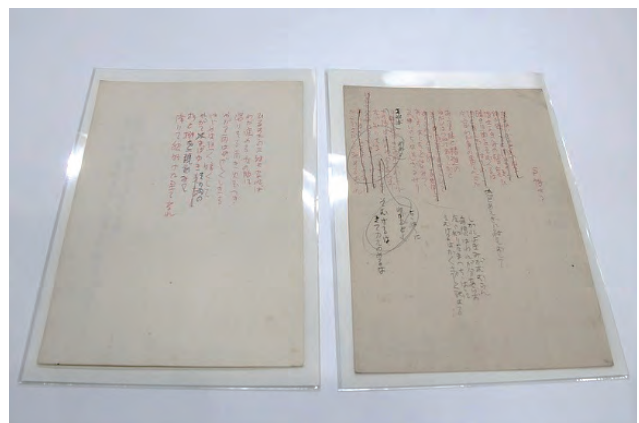


Figure 11 Draft of Kenji Miyazawa.



Figure 12 X-ray microanalyzer (XGT-9000).

## II Cooperation in Research of Vincent van Gogh’s Painting

Vincent van Gogh’s works have been the subject of various studies around the world and as part of a survey of Van Gogh’s paintings in the collection of the Pola Museum of Art in Hakone, we analyzed the composition of the paints used in the works.

Non-destructive and non-contact analysis methods are required for the analysis of art works such as paintings and photographs. In addition, it is difficult to take artworks out of the museum due to the security and storage environment, and rapid analysis is required. In order to meet these requirements, we modified the equipment so that it could analyze the paintings appropriately and installed it in the museum’s basement storage room for analysis. Based on the elements detected, we were able to estimate the type of paint that Van Gogh is believed to have used.

We will continue to contribute to the elucidation and preservation of cultural assets such as documents and paintings by measuring and analyzing their production dates and materials.



Figure 13 X-ray analyzer for large samples (XGT).

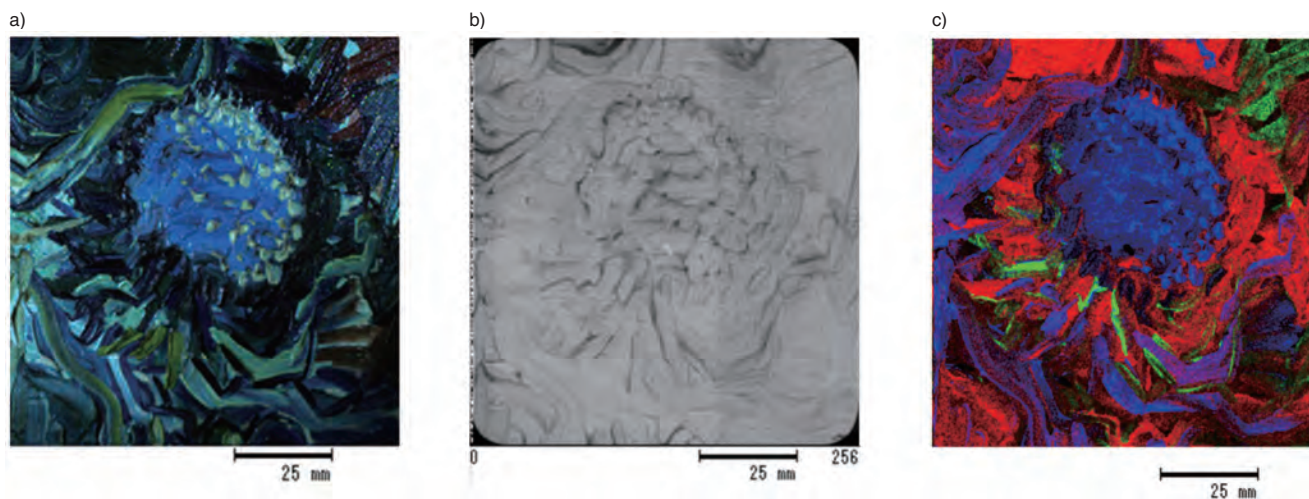


Figure 14 Mapping image (thistle flower; Vincent van Gogh)  
a) optical microscope image, b) X-ray transmission image, c) multilayer image (red: copper, green: iron, blue: zinc).

## JAXA Participates in the Initial Analysis Project of Hayabusa2

The asteroid Ryugu is thought to be a celestial body with information about the birth of the solar system approximately 4.6 billion years ago. The Japan Aerospace Exploration Agency (JAXA)’s “Hayabusa2” successfully completed its mission to bring back samples from Ryugu, and in June 2021, scientists from 14 countries around the world began the initial analysis. The initial analysis was conducted by six international teams (chemical analysis team, stone material analysis team, sand material analysis team, volatile components analysis team, solid organic material analysis team, and soluble organic material analysis team) over a period of about one year. HORIBA Techno Service belonged to the chemical analysis team and conducted analyses using a micro X-ray fluorescence spectrometer, a Raman microscope, and a carbon-sulfur

analyzer to elucidate the chemical properties of the Ryugu samples, including what elements were contained in what proportions and in what state of bonding.

In the initial analysis, it was necessary not only to perform the analysis with high precision, but also to minimize contamination of the sample for the next analysis team. Therefore, based on our accumulated analytical know-how, we developed a special container called a “cell” that is strong, sealed, and easy to handle. Using the developed cell, we were able to maintain optimum conditions for analysis and conduct nondestructive, non-contact analysis. Further investigations will be conducted by other teams to understand the nature and origin of Ryugu, and to unravel the mysteries of the origin and evolution of the solar system and life.



Figure 15 Measurement with Raman spectrometer.

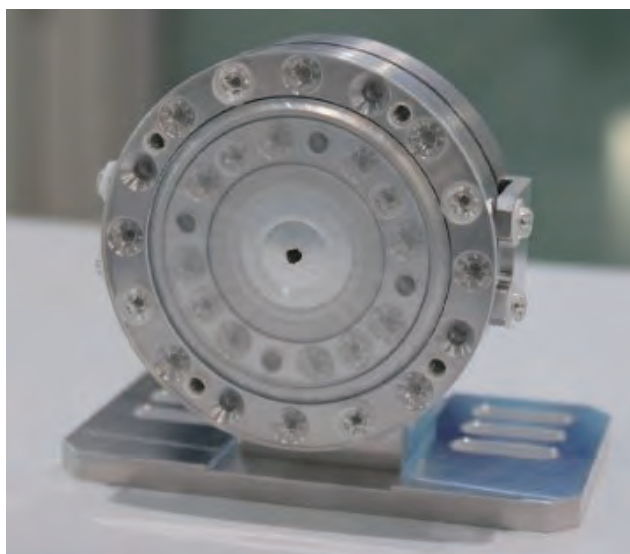


Figure 16 Cell for measurement.

## Conclusion

The above is an explanation of the newly established Analytical Solution Plaza and examples of solutions using HORIBA's analyzers. HORIBA Techno Service will continue to make every effort to help our customers realize their "understanding" by providing solutions through "measurement."

\* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.



**SAKAGUCHI Mai**

Analytical & Testing Technology Department  
Analytical Technology Division  
HORIBA Techno Service Co., Ltd.

# Facilities Introduction

## Introduction to HORIBA FRANCE Applications Laboratory: Missions and Resources

### Alessia QUATELA

HORIBA FRANCE SAS Applications Center has its main analysis laboratory located in Palaiseau, Île de France. The principal role of this laboratory is to exhibit and demonstrate the HORIBA's scientific instruments to further increase the level of customer focus and application support. The laboratory offers application support and full access to our knowledge base and instruments. The laboratory is staffed by an experienced applications team of MSc. and Ph.D. scientists with a variety of backgrounds including Analytical Chemistry, Pharma, Semiconductors, etc.

Welcome, your applications laboratory visit starts here.



## Our Missions:

- ✓ Samples analysis for potential customers
- ✓ Paid analysis for all the systems
- ✓ Live or remote demonstrations of instruments' operations
- ✓ Support to existing customers by phone, e-mail or face-to-face meeting
- ✓ After-purchase training on customer site, scheduled training on HORIBA FRANCE site or by remote
- ✓ Development of new analytical methods and procedures for and with our customers
- ✓ Participation at scientific collaborations
- ✓ Participation at conferences and workshops with talks and posters
- ✓ Validation of new products (accessories, software...)
- ✓ Writing technical (Application Notes and Peer Reviewed Articles), commercial and marketing documents
- ✓ Customers' visits for application support with Sales Forces/Product Specialists/Product Managers

## Material Resources:

The 250 m<sup>2</sup> laboratory hosts different techniques, from elemental analysis to molecular analysis, surface analysis and particle characterization: Atomic force microscopy (AFM), micro and macro-Raman, AFM-Raman, Fluorescence, C/S analyzer, X-Ray Fluorescence (XRF), Glow Discharge Optical Emission Spectroscopy (GD-OES), Inductive Coupled Plasma Optical Emission Spectrometry (ICP-OES), Laser diffraction (Particle Characterization Analysis-PCA), Spectroscopic ellipsometry, Surface Plasmon Resonance imaging (SPRi), etc. (Figure 1).

Here the potential customers have the possibility of testing the systems before the purchase, being trained by our experts (trainings are taught in English and/or in French) on the latest hardware and software releases, analyze their samples. The laboratory has also strong relationships with industry and academia and works in many collaborative projects:



Figure 1 HORIBA FRANCE Applications Laboratory.

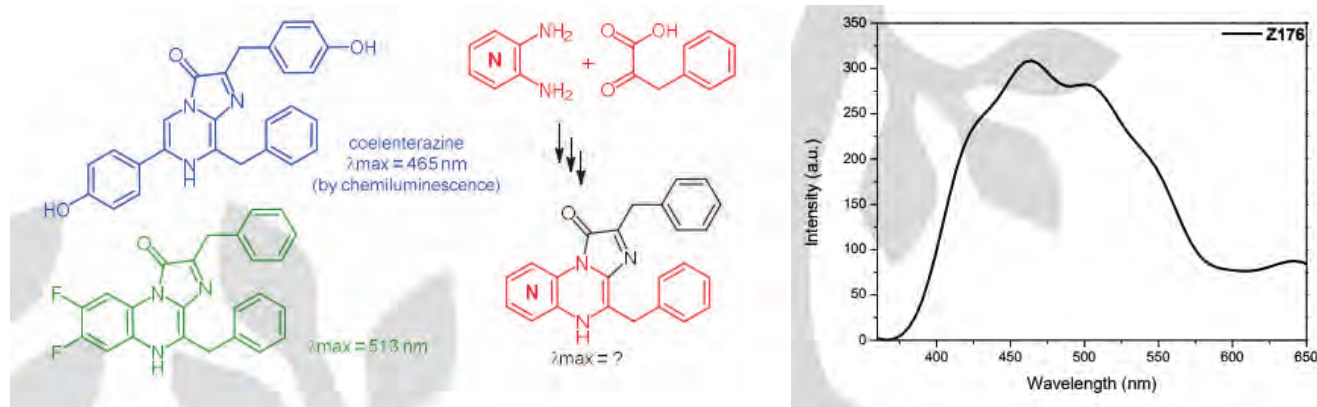


Figure 2 Chemiluminescence spectrum of an investigated compound.

- local collaborations with research centers located on the Plateau de Saclay, a new scientific and technological cluster inspired by the Silicon Valley

- regional and national collaborations with laboratories from various communities (semiconductor, H<sub>2</sub>, pharma, environment etc.)

- international collaborations as, just to mention one, the Harverstore project which received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 824072.

As an example of this scientific exchange, Dr. Y. Janin from Pasteur Institute contacted the Horiba application lab as he was looking for a system sensitive enough to detect the chemiluminescence/bioluminescence from luciferins molecules in the frame of the LuLISA project (*bioluminescence as a tool for human diagnostics, from allergy to Covid19*).

This research project aims developing diagnostic tools (i.e., serological tests) for multiple infectious diseases at local, regional or nation scales.

The use of the Aqualog was crucial to detect their weak signal and characterize this kind of molecules (Figure 2).

Two articles are the results of this fruitful collaboration:

- Gagnot G, Hervin V, Coutant EP, Goyard S, Jacob Y, Rose T, Hibti FE, Quatela A, Janin YL., *Core-Modified Coelenterazine Luciferin Analogues: Synthesis and Chemiluminescence Properties*, Chemistry 2021
- Gagnot G, Legrand P, Tadros A, Ezzhara-Hibti F, Quatela A, Janin YL., *On pyridopyrazinol chemistry, synthesis of chemiluminescent substances*, Synthesis 2021 Feb

## Human Resources:

Technical support is provided by Ph. D.s, MSc.s, and Master students. Senior scientists and market/technical experts from other departments supervise and support the application team and the customers' projects (Table 1).

Table 1 Experts' background summary

Technique	Background
AFM/Raman	Biophysics, Advanced Materials, Material Science, Pharma, Electronics/Semiconductors, Nano-optics, Nano-Science
C/S analyzer-GD	Material Science
Ellipsometry	Material Science
Fluorescence	Material Science, Biophysics, Cosmetics
ICP	Analytical Chemistry
PCA	Physics, AgroFood, Material Science
PP-TOFMS	Analytical Chemistry and Material Science
SPRi	Biology, Agro-food
XRF	Material Science

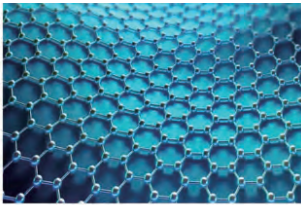
## Applications domains:

This wide background is daily employed to support our applications demand and the main applications trends (Figure 3).

The combination of our multidisciplinary experience and technical offer permits to propose to the customers a complete solution building trust, creating added value, and ensuring their satisfaction.

\*Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.





### Advanced Materials

- Energy
- Semiconductor
- Healthcare
- Quantum



### Water

- Treatment & Recycling
- Quality control
- Drinking water
- $\mu$ -plastics



### Life Sciences

- Agrofood & Botany
- Cosmetics
- Pharma
- Biology
- Medical



### Energy

- PV & Li battery
- Fuel cell
- Biofuel
- Hydrogen
- Flow &  $\mu$ -battery

Figure 3 Applications Mega Trends.



**Alessia QUATELA, Ph. D.**

Head of the Applications Laboratory  
HORIBA FRANCE SAS

# Facilities Introduction

## HORIBA Technical Centers at Premier Institutes in India

Dr. John Kiran ANTHONY

Dr. Rajeev GAUTAM

Dr. H.C. SUDEEKSHA

High-end instruments are indispensable tools in modern-day, cutting-edge research. While they are expected to add high value to the advanced research work, the understanding of potential of these sophisticated instruments for multiple applications plays a vital role in their wider usage. In a growing market like India, creating an effective awareness of such advanced equipment is the need of the hour to enhance HORIBA sales. In this direction, HORIBA India (HIN) Scientific had analysed the market situation to understand the existing distributor-driven sales picture and had realized that it was essential to create a suitable HORIBA-Academics-Industry platform to facilitate regular promotional activities to drive sales of all scientific products to both academic and industrial markets.

### Key words

research lab, analytical facility, HORIBA-IISc, HORIBA-IIT Delhi



### Introduction

The Indian analytical market analysis and customer voice indicated us a different way of branding by partnering with a few premier institutes in India that had their brand significance in both academic and industrial domains. The Indian Institute of Science (IISc) located in Bangalore emerged as our preferred institute because of various aspects of branding it would bring to HORIBA: IISc is the top-most influential academy of India that was initially started by Jamsetji TATA before it was handed over to the central government of India for making it a highly funded, rank-1 institute of India that attained global importance.

Prof. C.V. Raman served as the first Indian director of this institute. With a timely support and guidance of Prof. Siva Umopathy, the well-known Raman spectroscopist from this institute, HORIBA India (HIN) could sign an MoU with IISc for setting up the HORIBA-IISc Technical Center (HITC) in 2018. The HITC was inaugurated by Dr. Jai Hakhu, Prof. S Umopathy, Prof. S Ramakrishnan, Dr. Rajeev Gautam, and Prof. G Mugesh (from R to L), followed by a grand customer connect (Figure 1).

Notably, it was the first-ever step taken by HORIBA in India to start a technical platform, with its own Application Scientists, for running a customer-outreach program to

strengthen the direct marketing in India and SAARC (HIN secured a global HORIBA BlackJack award for this idea in 2019).



Figure 1 Indian Institute of Science, India's topmost research institute and a glimpse of the inaugural ceremony of the HITC.



Figure 2 A view of the present HITC.



## HITC strengthens the Industry-Academy relationship:

HITC is a state-of-the-art applications lab comprising LabRAM HR Evolution, Duetta, DeltaPro, and SZ-100 instruments, with the possibility of further expansion with other equipment for demonstration (Figure 2). In phase II, we are planning to showcase Aqualog, AFM-Raman, veterinary products, and Smart-Assay kits.

IISc scholars get free access to this analytical center and a chance to work with HORIBA scientists for their collaborative research. Through HITC, HORIBA gets the advantages of free access to all online literature, library, world-class faculty interaction and guidance. Our collaboration with Ph.D. and postdocs will create future potential customers. We are running various industrial projects to help sales of high-end techniques such as Raman, ViewSizer and Fluorescence. As IISc has several HORIBA customers on its campus, HIN can showcase

various other HORIBA techniques that are procured by IISc to prospective customers. Various industrial visitors at HITC get an opportunity to interact with both HIN Scientists as well as IISc faculty and HORIBA gets good chances for impressing these customers through faculty testimony and recommendation.

## Welfare to the HORIBA group:

Since its inception, the HITC has been catering to the needs of potential academic and industrial customers from both India and SAARC countries. The center is used for HIN internal team training, COE interactions, distributor training, and marcom materials creation (application notes/publications). Excited by the successful operation of this much-needed Industry-Academy platform, the present director of IISc has happily allotted a bigger space for HITC in the Chemical Sciences Block that is

ideally located adjacent to the nanoscience center, the physical science block, the biological science block, and the aero science block. This gives us ample opportunities for bringing multiple researchers to the HORIBA community. We already started witnessing the results in terms of various collaborations with the faculty of IISc (who chair various purchase committees in India) to boost cross-segment activities as well.

World-class scientists and researchers from academia and industry frequently visit IISc, so it is much easier for us to invite them to HITC to discuss their active research problems and the new technology or solutions they are looking for. Customer feedback on our products and service received during these interactions will strengthen our technical capabilities and customer engagement programs. Various research scholars are being trained by our Applications Scientists Dr. John Kiran Anthony and Dr. H. C. Sudeeksha to regularly

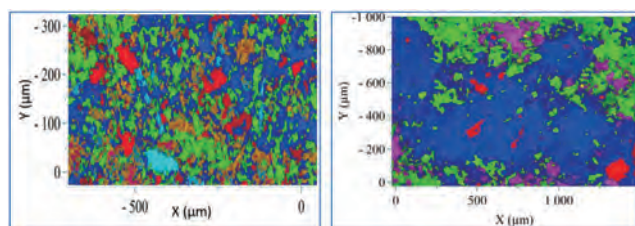


Figure 3 Raman images of finished tablets showing distribution of API (green) and excipients (colors) (a) and polymorphs of API polymorphs (red and blue) (b).

use all available instruments for their research work and to acknowledge HITC in their publications. Multiple projects in Raman, PCA and Fluorescence spectroscopy have been handled for pharmaceuticals, food, and battery industries. All potential customers are regularly invited for a demonstration at HITC, and this has served as a key factor in winning sales against our competitors! The customers see this joint venture between HORIBA and IISc as a confident technical platform, so that they consider HORIBA as their preferred partner. As a result, we see that many Contract Research Organizations (CROs) and 3<sup>rd</sup> Party Testing Labs have already started purchasing HORIBA equipment for their research and analysis work. This will open a potential market in pharma, biopharma, food, chemicals, metals, and cement in India for HORIBA products.

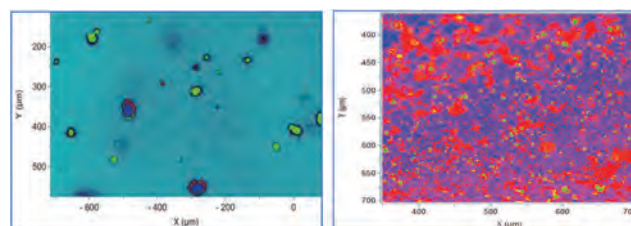


Figure 4 Polymorphs of API (blue, red, green) in skin cream (a) and distribution of fused graphene with silicon (red) graphene (blue) and silicon (green) on an electrode surface (b).

### Expansion and Way forward:

The presence of HITC in Bangalore has attracted customers from most parts of India, yet it is a bit distant for customers from North part of India. Encouraged by the success of HITC Bangalore, we have now signed an MOU with the Indian Institute of Technology (IIT) Delhi which is a prominent and influential technological institute located in Delhi (Figure 5). This center is currently hosting our LA-960V2 supervised by Application Scientist, Dr. Namrata Jain, who is offering hands-on trainings to potential customers and academic researchers. The center will soon be expanded as a technical hub for Scientific, Optical Smart Sensing, and Process and Environment divisions in the new campus of IIT D Sonipat.

HIN has witnessed several advantages of creating technical centers at these premier institutes in India. We plan to actively carry out our branding activities to enhance our



Figure 5 The MOU signing ceremony for HORIBA-IIT Delhi Technical Center.

market share and to create new domains of the market for the latest technologies of HORIBA.

\* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.



**Dr. John Kiran ANTHONY**  
Segment Head & Applications Scientist  
HORIBA Scientific India



**Dr. Rajeev GAUTAM**  
Corporate Officer  
HORIBA, Ltd., Japan  
President  
HORIBA India



**Dr. H.C. SUDEEKSHA**  
Applications Scientist  
HORIBA Scientific India

# Facilities Introduction

## Introduction of Application Centers in HORIBA China

### Jing SHEN

HORIBA Application centers in China have gone through different phases. All of them were dedicated to meet all requests from the Chinese market. At the same time, they are reference to show HORIBA capabilities on advanced techniques of optics and spectroscopy. In 2022, with the opening of Analytical Solution Plaza (ASP), the new era is coming.



### Introduction

In 2008, HORIBA Scientific settled its first demo system in Beijing. From that day, a new business mode started in China, with seeing is believing. In these early stages, customers were interested to see instruments specifications and reliable results from their own samples.

As, our business and customer base grew with time. In 2011, to better support our growth and our customer base, we expanded our capabilities in Beijing and opened a new application center in Shanghai. While, in Beijing, the application center was focused on demonstrating the performances of our Raman and Fluorescence systems, in Shanghai, our customers had access to most of our HORIBA Scientific products. At the same time, we grow the number of application engineer and their skills to provide regular training classes to our customers and education program to the next generation of customers. This

program based on optical technologies became popular in China under the name of HORIBA Optical School.

To increase our business, addressing industrial needs is required. Nowadays, we see an increasing demand from industry to provide solutions to different issues they are facing. Providing a solution means understanding the customer pains and having the capabilities to solve them in a short time.

Our company made a big strategic investment in China, by building a big facility in Shanghai, the HORIBA C-CUBE. In this new facility, a large area is dedicated to demonstrating all HORIBA technologies and to provide a series of solutions for current and future needs of the China Industry, named, Analytical Solution Plaza (ASP). The open ceremony is planned for this year. The ASP is an open space, designed to show in a glance for visitors, all HORIBA advanced techniques such as elemental



Figure 1 Application Center in Beijing.



Figure 2 Application Center in Shanghai.

analysis, molecular analysis, surface/coating analysis, particle size analysis etc. The ASP is divided into four markets area, Energy, Semiconductor, Environment, and Life Science, which are in line with both the China market trends and company megatrend directions. As example, clean energy is one of the key points to achieve the carbon peak and carbon neutrality. Lithium battery, hydrogen, solar cells are all playing a significant role. In ASP, the team will continue our mission to bring out solutions besides graphitization degree characterization for LiB materials, silicon crystallinity and thickness for solar cell, and so on.

These application solution examples will be shown briefly on digital panels in each relative area. Visitors can play

with the digital panels to understand HORIBA capabilities to solve their issues. The examples will grow with time by building collaborations with Key Opinion Leaders in the field of each application. To meet the local customization needs, the application team in ASP will work closely with Local Engineering team to fix the specifications and to evaluate the prototype. In such a way, customized solutions are provided to customers with China speed. With ASP, a close collaboration between HORIBA segments is expected to expand our offer and support our customers in semiconductors, automotive and environmental customers.

Let's light up a bright future with our ASP in HORIBA C-CUBE.



Figure 3 The entrance of ASP in HORIBA C-CUBE.

## HCT application center solution case examples

### Micro Fluorescence Solution for Perovskite based Solar Cell

Perovskite solar cells have become highly efficient nowadays. However, a number of challenges remain before they can become a competitive commercial technology, e.g. stability, scale, etc.

The film uniformity is one of the key specifications for perovskite solar cell produced by different processes. A good sample was acquired from one of the top labs for perovskite research in China. We made the investigation with Nanolog with CCD detector and microscope to see if there is any difference from the crystals and thus to check the film uniformity. Weak NIR emission was observed from the samples under microscope.

We made our first try to process the data with Labspec software. It is very interesting to get the distribution of peak position and peak width from the film on bare glass substrate. The peak position is different from different size and shape of the crystals. The FWHM distribution

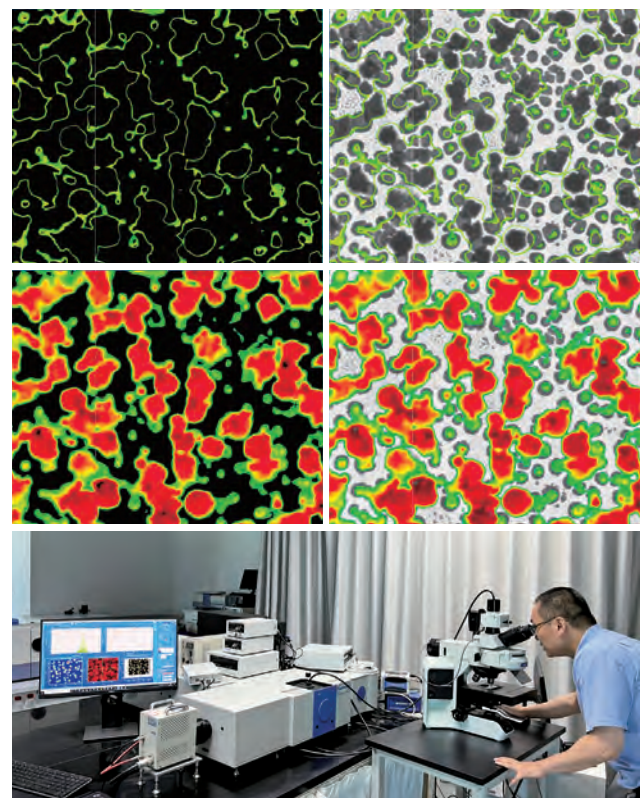


Figure 4 Peak position distributions and Nanolog.

images further confirm that the perovskite film is composed of different defected or non-uniform crystal forms. Lifetime mapping will be our next goal for this kind of sample.

### Solution with Multi Techniques for Archeology

Black-glazed porcelain, especially Jian (Tenmoku) wares, which are famous for their lustrous black glaze that exhibits unique colored patterns, is highly valued in China and other Asian countries.

In collaboration with SIOM, CAS, we had the chance to understand both the elemental and compositional information from black-glazed porcelain using XGT and Raman spectroscopy respectively.

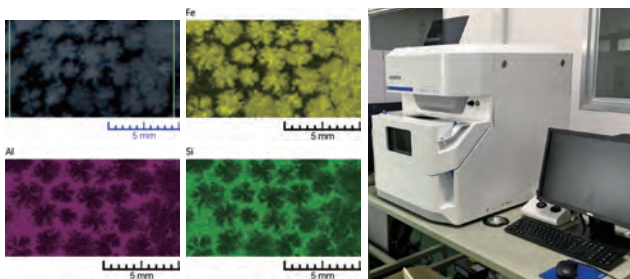


Figure 5 Fe, Al, Si distribution and XGT-9000.

It is well known that the black-glazed porcelain is iron rich. From XGT images, we can see a clear Fe precipitation on the silvery appearance of the snow like patterns.

Besides, it is interesting to know the phase of iron oxide which can well reveal the firing conditions and firing procedure of ancient ceramics.

With Raman analysis, it is found that the snow like patterns are composed of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and the dark background are composed of  $\epsilon\text{-Fe}_2\text{O}_3$  wherever it appears in crystal or non-crystal shape under microscope.

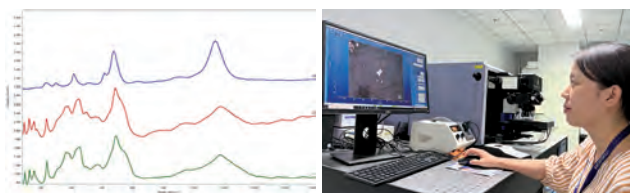


Figure 6  $\alpha\text{-Fe}_2\text{O}_3/\epsilon\text{-Fe}_2\text{O}_3$  spectra with LabRam Odyssey.

\* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.



**Jing SHEN, Ph. D.**  
 Application Department Manager  
 HORIBA Scientific  
 HORIBA China Trading Co., Ltd.





## Porosity and size analysis of porous microparticles by centrifugal sedimentation with and without density gradient

a: Yuichi Kato, Takushi Sugino, b: Takahiro Morimoto, Kazufumi Kobashi, Toshiya Okazaki, c: Tetsuji Yamaguchi, Tetsuya Mori

a: Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Kansai Center

b: CNT-Application Research Center, AIST

c: HORIBA, Ltd.

*Powder Technology* Volume 407, July 2022, 117663

## Determination of Cabernet Sauvignon wine quality parameters in Chile by Absorbance-Transmission and fluorescence Excitation Emission Matrix (A-TEEM) spectroscopy

a: Alvaro Gonzalez, Jorge Zincker, b: Adam Gilmore, Linxi Chen, ac: Doreen Schober

a: Center for Research and Innovation, Viña Concha y Toro, Ruta k-650 km 10, Penciahue, Chile

b: HORIBA Instruments Inc., 20 Knightsbridge Rd., Piscataway, NJ 08854, USA

c: Emiliana Organic Vineyards, Nueva Tajamar 481, Las Condes, Santiago, Chile

*Food Chemistry* Volume 392, 30 October 2022, 133101

## Overall equipment effectiveness, efficiency and slide review analysis of high-end hematology analyzers

a: Sukesh Chandran Nair Dr, Pandiyan Murugan, Asady Sukanya Sukumar, Joy J. Mammen, Saravanan Mullai

b: Shubham Rastogi

a: Department of Transfusion Medicine & Immunohematology, Christian Medical College, Vellore, Tamil Nadu, India

b: HORIBA Medical, HORIBA ABX SAS, Parc Euromédecine - Rue du Caducée, France

*Practical Laboratory Medicine* Volume 30, May 2022, e00275

## Safe extended-range cycling of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -based anodes for ultra-high capacity thin-film batteries

a: Valerie Siller, Juan Carlos Gonzalez-Rosillo, Marc Nuñez Eroles, Alex Morata, b: Michel Stchakovsky, cde: Raul Arenal

af: Albert Tarancón

a: Catalonia Institute for Energy Research (IREC)

b: HORIBA Scientific, Jobin Yvon

c: Instituto de Nanociencia y Materiales de Aragon (INMA)

d: Laboratorio de Microscopias Avanzadas (LMA)

e: Fundacion ARAID

f: Catalan Institution for Research and Advanced Studies (ICREA)

*Materials Today Energy* Volume 25, April 2022, 10097

## Perspectives for regulating 10 nm particle number emissions based on novel measurement methodologies

a: Z. Samaras, L. N.tziachristos, A.Kontses, Z.Toumasatos, A.Tsakis, b: M.Rieker, P.Kreutziger, c: E.Papaioannou, D.Zarvalis, P.Baltzopoulou, N.D.Vlachos, L.Chasapidis, D.Deloglou, E.Daskalos, d: W.F.van Dorp, e: M.Kousoulidou, f: J.Andersson, g: A. Bergmann, M.Bainschab, h: S.Hausberger, L.Landl, i: J.Keskinen, P.Karjalainen, S.Martikainen, j: A.Mamakos, k: Ch Haisch, l: O.Piacenza, G.Nicol, m: A.N.Bhave, K.F.Lee, no: J.Akroyd, nop: M.Kraft, q: M.Kazemimanesh, A.M.Boies, r: C.Focsa, D. Duca, Y. Carpentier, C.Pirim, s: J.A.Nobler, O.Lancry, S.Legendre, t: T.Tritscher, J.Spielvogel, H.G.Horn, u: A.Pérez, S.Paz, v: T.Lähde, A.Melas, cw: A.G.Konstandopoulos, x: S.Zinola, y: S.Di Iorio, F.Catapano, B.M.Vaglieco, z: H.Burtscher, aa: D.Zamora, ab: M.Maggiore

a: Aristotle University, Lab of Applied Thermodynamics  
 b: HORIBA Europe GmbH  
 c: Centre for Research and Technology-Hellas (CERTH)  
 d: Uniresearch B.V.  
 e: European Climate, Infrastructure and Environment Executive Agency  
 f: Ricardo Automotive & Industrial, Shoreham Technical Centre  
 g: University of Technology Graz, Institute of Electronic Sensor Systems  
 h: University of Technology Graz, Institute for Internal Combustion Engines and Thermodynamics  
 i: Tampere University, Aerosol Physics Laboratory  
 j: AVL List GmbH  
 k: Technical University of Munich  
 l: Centro Ricerche Fiat  
 m: CMCL Innovations  
 n: Department of Chemical Engineering and Biotechnology, University of Cambridge  
 o: CARES, Cambridge Centre for Advanced, Research and Education in Singapore  
 p: School of Chemical and Biomedical Engineering, Nanyang Technological University  
 q: University of Cambridge, Department of Engineering,  
 r: Univ. Lille  
 s: HORIBA France SAS  
 t: TSI GmbH  
 u: IDIADA Automotive Technology SA  
 v: European Commission, Joint Research Centre (JRC)  
 w: Department of Chemical Engineering, Aristotle University Thessaloniki  
 x: IFP Energies Nouvelles, Institut Carnot IFPEN Transports Energie  
 y: Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili STEMS  
 z: Institute for Sensors and Electronics  
 aa: Mobility Ion Technologies SL (MION)  
 ab: Directorate General for Research and Innovation  
*Journal of Aerosol Science* Volume 162, May 2022, 105957

## Facile fabrication of 2D material multilayers and vdW heterostructures with multimodal microscopy and AFM characterization

ab: Siyan Dong, S. Shiva. P. Nathamgari, Xu Zhang, Jin Wook Hwang, Horacio D. Espinosa, c: Xiang Zhang, Pulickel M.Ajayan, d: Andrey Krayev

a: Department of Mechanical Engineering, Northwestern University  
 b: Theoretical and Applied Mechanics Program, Northwestern University  
 c: Department of Materials Science and NanoEngineering, Rice University  
 d: HORIBA Scientific, Novato  
*Materials Today* Volume 52, January–February 2022, Pages 31-42

### A taxonomy of validation strategies to ensure the safe operation of highly automated vehicles

ab: Felix Batsch, a: Stratis Kanarachos, Mike Blundella, b: Madeline Cheah, Roberto Ponticelli

a: Institute for Future Transport and Cities, Coventry University,

b: Horizon Scanning Department, HORIBA MIRA

*Journal of Intelligent Transportation Systems* Volume 26, Issue 1, 2022, Pages 14-33

### Effects of aging time in hydrogen peroxide-glycine-based Cu CMP slurry

a: Juhwan Kim, Donggeon Kwak, c: Jungjae Park, Takayuki Kubota, ab: Taesung Kim

a: School of Mechanical Engineering, Sungkyunkwan University

b: SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University

c: HORIBA STEC KOREA

*Materials Science in Semiconductor Processing* Volume 140, 15 March 2022, 106343

### Multi-task manifold learning for small sample size datasets

a: Hideaki Ishibashi, Tetsuo Furukawa, ab: Kazushi Higa

a: Kyushu Institute of Technology

b: HORIBA Ltd.

*Neurocomputing* Volume 473, 7 February 2022, Pages 138-157

### Evidence for 3-D network of P-centered pyramidal $P(\text{Se}_{1/2})_3$ and quasi-tetrahedral $\text{Se}=\text{P}(\text{Se}_{1/2})_3$ local structures and their 3-membered ring super structure counterparts decoupled from quasi 1D- ethylene-like $\text{P}_2\text{Se}_{2+x}$ ( $x = 2, 1, 0$ ) chains in $\text{P}_x\text{Se}_{100-x}$ glasses

a: Matthew Burger, Aaron Welton, Maxwell McDonald, Ralph Chbeir, P. Boolchand, b: Soumendu Chakravart, c: Badriah S. Almutairi, d: S. Mamedov

a: Department of Electrical Engineering and Computer Science, University of Cincinnati

b: Department of Mechanical and Materials Engineering, University of Cincinnati

c: Department of Physics, College of Sciences, Princess Nourah bint Abdulrahman University

d: HORIBA Instruments Incorporated

*Journal of Alloys and Compounds* Volume 895, Part 2, 25 February 2022, 162645

### Diagnostic moléculaire « Point-of-care » innovant pour la détection rapide des arbovirus

a: Fanny Leon, Elena Pinchon, Charly Mayran, Jean-François Cantaloube, Philippe Van De Perre, Jean-Pierre Moles, Chantal Fournier-Wirth, b: Aurélien Daynes, c: Kenza Behlaj

a: Pathogénèse et Contrôle des Infections Chroniques et Emergentes (EFS-Inserm-Université de Montpellier-Université des Antilles)

b: HORIBA Medical, France

c: EFS, La Plaine Saint-Denis, France

*Transfusion Clinique et Biologique* Volume 28, Issue 4, Supplement, November 2021, Page S33

## An Interlaboratory Comparison on the Characterization of a Sub-micrometer Polydisperse Particle Dispersion

a: Kurt D.Benkstein, Dean C. Ripple, b: Gurusamy Balakrishnan, c: Ashwinkumar Bhirde, d: Pascal Chalus, Atanas Koulov, Anja Matter, e: Tapan K.Das, Sambit R.Kar, f: Ngoc Do, g: David L.Duewer, h i: Nazar Filonov, j: Fook Chiong Cheong, Laura A. Philips, k: Patrick Garidel, Franziska Schleinzer, l: Nicole S.Gill, Heather Anne Wright, m n: Adam D.Grabarek, o: David G.Grier, Andrew D.Hollingsworth, p: Judith Hadley, q: Wesley W.Howard, Harshit Khansa, Yoen Joo Kim, r: Maciej Jarzębski, s: Wim Jiskoot, Stefan Romeijn, t: Vikram Kestens, Yannic Ramaye, u: Christine Probst, v: Theodore W.Randolph, Jared R.Snell, w: Miguel Saggu, x: Jan “Kuba” Tatarkiewicz, y: Dennis T.Yang

a: Biomolecular Measurement Division, National Institute of Standards and Technology, USA

b: Analytical Development and Attribute Science, Bristol Myers Squibb, USA

c: Office of Biotechnology Products, Office of Pharmaceutical Quality, Center for Drug Evaluation and Research, USA

d: Lonza AG, Drug Product Services, Switzerland

e: Biologics Development, Bristol Myers Squibb, USA

f: Spectradyne LLC, USA

g: Chemical Sciences Division, National Institute of Standards and Technology, USA

h: AlphaNanoTech, USA

i: Particle Metrix, USA

j: Spheryx, Inc., USA

k: Boehringer Ingelheim Pharma GmbH & Co. KG, Germany

l: Yokogawa Fluid Imaging Technologies, USA

m: Coriolis Pharma, Germany

n: Division of BioTherapeutics, Leiden Academic Centre for Drug Research, Leiden University, Netherlands

o: Department of Physics and Center for Soft Matter Research, New York University

p: Malvern Pananalytical, USA

q: Analytical Sciences, BioPharmaceuticals Development, R&D, AstraZeneca, USA

r: Department of Physics and Biophysics, Faculty of Food Science and Nutrition, Poznan University of Life Sciences, Poland

s: Division of BioTherapeutics, Leiden Academic Centre for Drug Research, Leiden University, Netherlands

t: European Commission, Joint Research Centre (JRC), Belgium

u: Luminex Corporation, USA

v: Department of Chemical and Biological Engineering, University of Colorado

w: Pharmaceutical Development, Genentech, USA

x: HORIBA Instruments Incorporated

y: Biopharmaceutical Research and Development, Lilly Research Laboratories, Eli Lilly and Company, USA

*Journal of Pharmaceutical Sciences* *Journal of Pharmaceutical Sciences* Volume 111, Issue 3, March 2022, Pages 699-709

## Validation d'un automate d'hématologie destiné aux contrôles des produits sanguins

a: Nadine Marpoux, Fabien Lejarre, Francine Garnache, Christophe Besiers, b: Benjamin Rey, c: Gilles Dor

a: EFS Bourgogne Franche-Comté

b: Faculté de pharmacie, université de Strasbourg

c: Société HORIBA Medical

*Transfusion Clinique et Biologique* Volume 28, Issue 4, Supplement, November 2021, Page S63

### Development of Ag and Ag alloys-precipitated Ag<sub>2</sub>O-TeO<sub>2</sub> glass and Ag<sub>2</sub>O-TeO<sub>2</sub> glass/stainless steel reference electrodes for pH sensors

a: Tadanori Hashimoto, Keisuke Nakade, Atsushi Ishihara, b: Yuji Nishio

a: Division of Chemistry for Materials, Graduate School of Engineering, Mie University

b: HORIBA Advanced Techno, Co., Ltd.

*Sensors and Actuators B: Chemical* Volume 348, 1 December 2021, 130540

### Bipolar self-doping in ultra-wide bandgap spinel ZnGa<sub>2</sub>O<sub>4</sub>

a: Z.Chi, Wu C.Sartel, I.Madaci, V.Sallet, Y.Dumont, E.Chikoidze, b: Fu-Gow Tarntair, R.H.Horng, c: M.Frégnaux, d: Wan-Yu, e: P.Chapon, f: A.Pérez-Tomás

a: Groupe d'Etude de la Matière Condensée (GEMaC)

b: Institute of Electronics, National Yang Ming Chiao Tung University

c: Institut Lavoisier de Versailles (ILV), Université Paris-Saclay

d: Department of Materials Science and Engineering, Da-Yeh University

e: HORIBA Jobin Yvon SAS

f: Catalan Institute of Nanoscience and Nanotechnology (ICN2)

*Materials Today Physics* Volume 20, September 2021, 100466

### Yawn-like behavior in captive common bottlenose dolphins (*Tursiops truncatus*)

a: Akiko Enokizu, Tadamichi Morisaka, Motoi Yoshioka, b: Katsushi Murakami, Natsuko Sakurai, c: Nahoko Ueda

a: Graduate School of Bioresources, Mie University

b: Minamichita Beachland Aquarium

c: HORIBA Ltd.

*Behavioural Processes* Volume 189, August 2021, 104444

### Spectrofluorometric analysis combined with machine learning for geographical and varietal authentication, and prediction of phenolic compound concentrations in red wine

a: Ranaweera K.R. Ranaweera, b: Adam M. Gilmore, ac: Dimitra L. Capone, Susan E.P. Bastian, David W. Jeffery

a: Department of Wine Science and Waite Research Institute, The University of Adelaide (UA)

b: HORIBA Instruments Inc.

c: Australian Research Council Training Centre for Innovative Wine Production

*Food Chemistry* Volume 361, 1 November 2021, 130149

### Screening for potential interaction partners with surface plasmon resonance imaging coupled to MALDI mass spectrometry

a: Ulrike Anders, Renato Zenobi, ab: Maya Gulotti-Georgiev, b: Susann Zelger-Paulus, Roland K.O. Sigel, c: Fatima-Ezzahra Hibti, Chiraz Frydman, d: Detlev Suckau

a: Department of Chemistry and Applied Biosciences, ETH Zurich,

b: Department of Chemistry, University of Zurich

c: HORIBA France S.A.S

d: Bruker Daltonics

*Analytical Biochemistry* Volume 624, 1 July 2021, 114195

### Magnetic field-enhanced agglutination as a readout for rapid serologic assays with human plasma

a: Nevzat Temurok, Martine Clot, Aurélien Daynès, b: Fanny Leon, Elena Pinchon, Vincent Foulongne, Jean-François Cantaloube, Philippe Vande Perre, Chantal Fournier-Wirth, Jean-Pierre Molès

a: HORIBA ABX SAS

b: Pathogénèse et Contrôle des infections chroniques et émergentes, Université de Montpellier

*Talanta* Volume 233, 1 October 2021, 122407

### Time-resolved and excitation-emission matrix luminescence behaviour of boro-silicate glasses doped with Eu<sup>3+</sup> ions for red luminescent application

a: S.H. Nandyala, A. Stamboulis, b: G. Hungerford, c: J.D. Santos, d: B.M. Walsh, e: L. Di Silvio

a: School of Metallurgy and Materials, University of Birmingham

b: HORIBA Jobin Yvon IBH Ltd

c: REQUIMTE/LAQV –Departamento de Eng Metalúrgica e Materiais, Faculdade de Engenharia, Universidade do Porto

d: NASA Langley Research Center, Hampton

e: Faculty of Dentistry, Oral & Craniofacial Sciences, King's College London

*Materials Research Bulletin* Volume 140, August 2021, 111340

### Fluorescence Anisotropy Eems: Adding a New Dimension to the Study of Protein Local Environment

Karen E.Gall, Alex Siemiarczuk

HORIBA Scientific, Piscataway

*Biophysical Journal* Volume 120, Issue 3, Supplement 1, 12 February 2021, Page 117a

### Optimizing Model Calibrations for Natural Product Chemical Compositions with Absorbance-Transmittance Excitation-Emission (A-TEEM) Spectroscopy

Adam M.Gilmore

HORIBA Instruments Inc.

*Biophysical Journal* Volume 120, Issue 3, Supplement 1, 12 February 2021, Page 264a

### Dynamic impact of cellulose and readily biodegradable substrate on oxygen transfer efficiency in sequencing batch reactors

a: Ahmed Shawki Ahmed, b: Ahmed Khalil, c: Yuichi Ito, d: Mark C.M.van Loosdrecht, e: Domenico Santoro, fg: Diego Rosso, ah: George Nakhla

a: Department of Civil and Environmental Engineering, Western University  
b: Department of Mechanical and Materials Engineering, Western University  
c: HORIBA Advanced Techno,Co. Ltd.  
d: Dept. Biotechnology, Delft University of Technology  
e: USP Technologies  
f: Department of Civil and Environmental Engineering, University of California  
g: Water-Energy Nexus Center, University of California  
h: Department of Chemical and Biochemical Engineering, Western University  
*Water Research* Volume 190, 15 February 2021, 116724

### A label-free, direct solid-phase fluorimetric analysis of ochratoxin A in agricultural products with monoclonal antibody-immobilized monolith

ab: Koji Kikukawa, b: Miki Fukui, Ayano Oka, Ryohei Yamamoto, Atsushi Yamamoto, c: Mikiko Uchigashima, Takeshi Kono, d: Daisuke Kozaki, e: Shuji Kodama

a: Food Analysis Technology Center SUNATEC  
b: College of Bioscience and Biotechnology, Chubu University  
c: HORIBA, Ltd.  
d: Department of Chemistry and Biotechnology, Faculty of Science and Technology, Kochi University  
e: School of Science, Tokai University  
*Food Chemistry* Volume 346, 1 June 2021, 128736

### Sm<sup>3+</sup>-doped strontium barium borate phosphor for white light emission: Spectroscopic properties and Judd–Ofelt analysis

a: Sunil Thomas, Naser Qamhieh, Saleh T. Mahmoud, bc: Rani George, d: K.G. Gopchandran, e: Alessia Quatela

a: Department of Physics, UAE University  
b: Department of Physics, St. Aloysius College  
c: School of Pure and Applied Physics, Mahatma Gandhi University  
d: Department of Optoelectronics, University of Kerala,  
e: HORIBA France SAS  
*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* Volume 248, 5 March 2021, 119187

### Authentication of the geographical origin of Australian Cabernet Sauvignon wines using spectrofluorometric and multi-element analyses with multivariate statistical modelling

a: Ranaweera K.R. Ranaweera, b: Adam M. Gilmore, ac: Dimitra L. Capone, Susan E.P. Bastian, David W. Jeffery

a: Department of Wine and Food Science, and Waite Research Institute, The University of Adelaide (UA)  
b: HORIBA Instruments Inc, Piscataway  
c: Australian Research Council Training Centre for Innovative Wine Production  
*Food Chemistry* Volume 335, 15 January 2021, 127592



## Green production of limonene diepoxide for potential biomedical applications

abc: Anderson J. Bonon, bc: Juliana O. Bahú, Rubens Maciel Filho, b: Bruno C. Klein, d: Dalmo Mandelli

a: HORIBA Scientific, Irvine

b: Laboratory of Optimization, Design and Advanced Control (LOPCA) – University of Campinas

c: INCT-Biofabris – University of Campinas, School of Chemical Engineering

d: Center of Natural and Human Sciences, Federal University of ABC

*Catalysis Today* Volumes 388–389, 1 April 2022, Pages 288-300

\*Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.

# HORIBA World-Wide Network

## JAPAN

### HORIBA, Ltd.

2 Miyano Higashi-cho, Kisshoin, Minami-ku, Kyoto, 601-8510, Japan

Phone : (81)75-313-8121 Fax : (81)75-321-8312

#### Biwako Factory

1-15-1, Noka, Otsu, Shiga, 520-0102, Japan  
Phone : (81)-77-548-6130 Fax : (81)-77-548-6193

#### Tokyo Sales Office

Kanda Awaji-cho Nichome Building, 2-6 Kanda Awaji-cho, Chiyoda-ku, Tokyo, 101-0063, Japan  
Phone : 81-3-6206-4721 Fax : 81-3-6206-4730

#### Hokkaido Sales Office

6F Park East Sapporo, 1-3 Minami Ichijo Higashi, Chuo-ku, Sapporo, Hokkaido, 060-0051, Japan  
Phone : 81-11-207-1800 Fax : 81-11-207-1802

#### Tohoku Sales Office

4-21-8 Izumichuo, Izumi-ku, Sendai, Miyagi, 981-3133, Japan  
Phone : 81-22-776-8251 Fax : 81-22-772-6727

#### Tochigi Sales Office

1F Flora Building, 1-9-15 Higashishukugo, Utsunomiya, Tochigi, 321-0953, Japan  
Phone : 81-28-634-7051 Fax : 81-28-634-6099

#### Yokohama Sales Office

1F ShinYokohama Mineta Building, 2-3-19 Shinyokohama, Kohoku-ku, Yokohama, 222-0033, Japan  
Phone : 81-45-478-7017 Fax : 81-45-478-7029

#### Nagoya Sales Office

4F BIZrium Nagoya, 3-1-17 Noritakeshinmachi, Nishi-ku, Nagoya, Aichi, 451-0051, Japan  
Phone : 81-52-433-3450 Fax : 81-52-433-3460

#### Toyota Sales Office

2-23 Tsukasa-cho, Toyota, Aichi, 471-0831, Japan  
Phone : 81-565-37-8510 Fax : 81-565-37-8511

#### Hamamatsu Sales Office

221-1 Sanjino-cho, Minami-ku, Hamamatsu, Shizuoka, 430-0816, Japan  
Phone : 81-53-468-7780 Fax : 81-53-468-7781

#### Osaka Sales Office

4F ShinOsaka UenoToyo Building, 7-4-17 Nishinakajima, Yodogawa-ku, Osaka, 532-0011, Japan  
Phone : 81-6-6390-8011 Fax : 81-6-6390-8012

#### Shikoku Sales Office

9-9 Imazato-cho, Takamatsu, Kagawa, 760-0078, Japan  
Phone : 81-87-867-4800 Fax : 81-87-867-4801

#### Hiroshima Sales Office

1F Furuta Building, 2-5-27 Miyanomachi, Fuchu-cho, Aki-gun, Hiroshima, 735-0005, Japan  
Phone : 81-82-288-4433 Fax : 81-82-286-0761

#### Kyusyu Sales Office

1F Hakata Fukoku Seimei Building, 8-30 Tenyamachi, Hakata-ku, Fukuoka, 812-0025, Japan  
Phone : 81-92-292-3593 Fax : 81-92-292-3594

#### Tokyo Branch

Kanda Awaji-cho Nichome Building, 2-6 Kanda Awaji-cho, Chiyoda-ku, Tokyo, 101-0063, Japan  
Phone : 81-3-6206-4711 Fax : 81-3-6206-4720

#### HORIBA Advanced Technology Center

11-5 Hokotate-cho, Kamitoba, Minami-ku, Kyoto, 601-8116, Japan  
Phone : 81-75-693-2300 Fax : 81-75-693-2350

#### Kutsuki Training Center

335-10 Tochu, Kutsuki, Takashima, Shiga, 520-1425, Japan  
Phone : 81-740-38-3127 Fax : 81-740-38-3126

#### Saiin Factory

43-1 Nishimizosaki-cho, Saiin, Ukyo-ku, Kyoto, 615-0046, Japan  
Phone : 81-75-323-7067 Fax : 81-75-323-7085

### HORIBA STEC, Co., Ltd.

11-5 Hokotate-cho, Kamitoba, Minami-ku, Kyoto, 601-8116, Japan

Phone : (81)-75-693-2300 Fax : (81)-75-693-2350

#### Aso Factory

Torikokogyodanchi, 358-11, Koumaibata, Toriko, Nishiharamura, Aso-gun, Kumamoto, 861-240, Japan  
Phone : (81)-96-279-2921 Fax : (81)-96-279-3364

#### Fukuchiyama Technology Center

11-1 Miwa-cho Miwa, Fukuchiyama, Kyoto, 620-1445 Japan  
Phone : (81)-773-59-2070 Fax : (81)-773-59-2074

#### Tokyo Sales Office

5F Kanda Awaji-cho Nichome Building, 2-6 Kanda Awaji-cho, Chiyoda-ku, Tokyo, 101-0063, Japan  
Phone : 81-3-6206-4731 Fax : 81-3-6206-4740

#### Tohoku Sales Office

4-21-8 Izumichuo, Izumi-ku, Sendai, Miyagi, 981-3133, Japan  
Phone : 81-22-772-6717 Fax : 81-22-772-6727

#### Yamanashi Sales Office

3F Daita Building, 2-14-13, Marunouchi, Kofu, Yamanashi, 400-0031, Japan  
Phone : 81 55-231-1351 Fax : 81- 55-231-1352

#### Nagoya Sales Office

4F BIZrium Nagoya, 3-1-17 Noritakeshinmachi, Nishi-ku, Nagoya, Aichi, 451-0051, Japan  
Phone : 81-52-433-3451 Fax : 81-52-433-3461

#### Kyushu Chuo Sales Office

Torikokogyodanchi, 358-11 Koumaibata, Toriko, Nishiharamura, Aso-gun, Kumamoto, 861-2401, Japan  
Phone : 81-96-279-2922 Fax : 81-96-279-3364

### HORIBA Advanced Techno, Co., Ltd.

2 Miyano Higashi-cho, Kisshoin, Minami-ku, Kyoto, 601-8551, Japan  
Phone : (81)-75-321-7184 Fax : (81)-75-321-7291

#### Factory

2 Miyano Higashi-cho, Kisshoin, Minami-ku, Kyoto, 601-8551, Japan  
Phone : 81-75-321-1215 Fax : 81-75-321-1079

#### Tokyo Sales Office

Kanda Awaji-cho Nichome Building, 2-6 Kanda Awaji-cho, Chiyoda-ku, Tokyo, 101-0063, Japan  
Phone : 81-3-6206-4751 Fax : 81-3-6206-4760

#### Tohoku Sales Office

4-21-8 Izumichuo, Izumi-ku, Sendai, Miyagi, 981-3133, Japan  
Phone : 81-22-776-8253 Fax : 81-22-772-6727

#### Nagoya Sales Office

4F BIZrium Nagoya, 3-1-17 Noritakeshinmachi, Nishi-ku, Nagoya, Aichi, 451-0051, Japan  
Phone : 81-52-433-3452 Fax : 81-52-433-3462

#### Osaka Sales Office

4F ShinOsaka UenoToyo Building, 7-4-17 Nishinakajima, Yodogawa-ku, Osaka, 532-0011, Japan  
Phone : 81-6-6390-8211 Fax : 81-6-6390-8222

#### Shikoku Satellite Office

9-9 Imazato-cho, Takamatsu, Kagawa, 760-0078, Japan  
Phone : 81-87-867-4841 Fax : 81-87-867-4842

#### Kyusyu Sales Office

1F Hakata Fukoku Seimei Building, 8-30 Tenyamachi, Hakata-ku, Fukuoka, 812-0025, Japan  
Phone : 81-92-292-3595 Fax : 81-92-292-3596

#### Kyushu Chuo Sales Office

Torikokogyodanchi, 358-11, Koumaibata, Toriko, Nishiharamura, Aso-gun, Kumamoto, 861-240, Japan  
Phone : 81-96-234-8035 Fax : 81-75-321-7291

### HORIBA TECHNO SERVICE Co., Ltd.

2 Miyano Higashi, Kisshoin, Minami-ku, Kyoto, 601-8305, Japan  
Phone : (81)-75-313-8125 Fax : (81)-75-321-5647

#### Tokyo Service Station

4F Kanda Awaji-cho Nichome Building, 2-6 Awaji-cho, Kanda, Chiyoda-ku, Tokyo, 101-0063, Japan  
Phone : 81-3-6206-4750 Fax : 81-3-6206-4742

#### Hokkaido Service Station

6F Park East Sapporo, 1-3 Minami Ichijo Higashi, Chuo-ku, Sapporo, Hokkaido, 060-0051, Japan  
Phone : 81-11-207-1801 Fax : 81-11-207-1802

#### Tohoku Service Station

4-21-8 Izumichuo, Izumi-ku, Sendai, Miyagi, 981-3133, Japan  
Phone : 81-22-776-8252 Fax : 81-22-772-6727

#### Fukushima Service Station

101 Office Tatsumi, 5-13-17 Saikon, Koriyama, Fukushima, 963-8862, Japan  
Phone : 81-24-925-9311 Fax : 81-24-925-9312

#### Tochigi Service Station

1F Flora Building, 1-9-15 Higashishukugo, Utsunomiya, Tochigi, 321-0953, Japan  
Phone : 81-28-634-6098 Fax : 81-28-634-6099

#### Chiba Service Station

1-8-12 Goichuo-higashi, Ichihara, Chiba, 290-0054, Japan  
Phone : 81-436-24-3914 Fax : 81-436-24-0642

#### Kashima Service Station

1-4-35 Kamisu, Kamisu, Ibaraki, 314-0143, Japan  
Phone : 81-299-91-0808 Fax : 81-299-92-9561

#### Tsukuba Service Station

1F Tsukuba Koken Building, 2-1-13 Umezono, Tsukuba, Ibaraki, 305-0045, Japan  
Phone : 81-29-863-7311 Fax : 81-29-859-5221

#### Saitama Service Station

1F Higashikawaguchi Garden Plaza, 1-6-1 Totsukahigashi, Kawaguchi, Saitama, 333-0802, Japan  
Phone : 81-48-298-6871 Fax : 81-48-298-6880

#### Nishitokyo Service Station

1F The-Macrocosm, 3-37-34 Izumi, Kokubunji, Tokyo, 185-0024, Japan  
Phone : 81-42-322-3211 Fax : 81-42-322-3210

#### Yokohama Service Station

1F Piime ShinYokohama Building, 2-3-19 Shinyokohama, Kohoku-ku, Yokohama, Kanagawa, 222-0033, Japan  
Phone : 81-45-478-7018 Fax : 81-45-478-7029

#### Fuji Service Station

1F Suzuki Building, 4-7 Suzukawahigashi-cho, Fuji, Shizuoka, 417-0012, Japan  
Phone : 81-545-33-3152 Fax : 81-545-33-3159

#### Hamamatsu Service Station

221-1 Sanjino-cho, Minami-ku, Hamamatsu, Shizuoka, 430-0816, Japan  
Phone : 81-53-464-1339 Fax : 81-53-464-6528

#### Tokai Service Station

2-23 Tsukasa-cho, Toyota, Aichi, 471-0831, Japan  
Phone : 81-565-37-3510 Fax : 81-565-37-3520

#### Nagoya Service Station

1F Riverpage, 3-203 Kamiyashiro, Meito-ku, Nagoya, Aichi, 465-0025, Japan  
Phone : 81-52-705-0711 Fax : 81-52-705-0710

#### Hokuriku Service Station

10-14 Imaizumiseibu-cho, Toyama, 939-8281, Japan  
Phone : 81-76-422-6112 Fax : 81-76-422-6446

#### Mie Service Station

1F Taiyo-Seimei Yokkaichi Building, 1-1-18 Unomori, Yokkaichi, Mie, 510-0074, Japan  
Phone : 81-59-340-6061 Fax : 81-59-340-6063

#### Kyoto Service Station

2 Miyano Higashi, Kisshoin, Minami-ku, Kyoto, 601-8305, Japan  
Phone : 81-75-325-5291 Fax : 81-75-321-5647

#### Osaka Service Station

4F ShinOsaka UenoToyo Building, 7-4-17 Nishinakajima, Yodogawa-ku, Osaka, 532-0011, Japan  
Phone : 81-75-325-5291 Fax : 81-75-321-5647

#### Hyogo Service Station

381 Nniyo, Himeji, Hyogo, 670-0952, Japan  
Phone : 81-79-284-8320 Fax : 81-79-284-8321

#### Shikoku Service Station

9-9 Imazato-cho, Takamatsu, Kagawa, 760-0078, Japan  
Phone : 81-87-867-4821 Fax : 81-87-867-4822

#### Okayama Service Station

1-12-35 Tsurajima, Kurashiki, Okayama, 712-8012, Japan  
Phone : 81-86-448-9760 Fax : 81-86-446-5637

#### Hiroshima Service Station

1F Furuta Building, 2-5-27 Miyanomachi, Fuchicho, Aki-gun, Hiroshima, 735-0005, Japan  
Phone : 81-82-283-3378 Fax : 81-82-286-0761

#### Yamaguchi Service Station

1F 3rd Hanada Building, 1-72 Hashimoto, Shunan, Yamaguchi, 745-0022, Japan  
Phone : 81-834-34-8684 Fax : 81-834-34-8685

#### Kyusyu Service Station

1F Hakata Fukoku Seimei Building, 8-30 Tenyamachi, Hakata-ku, Fukuoka, 812-0025, Japan  
Phone : 81-92-292-3597 Fax : 81-92-292-3598

#### Oita Service Station

1F Tsuruwa Building, 2-2-37 Hagiwara, Oita, 870-0921, Japan  
Phone : 81-97-551-3982 Fax : 81-97-551-3889

#### Kumamoto Service Station

Toriko-kogyodanchi, 358-11, Koumaibata, Toriko, Nishiharamura, Aso-gun, Kumamoto, 861-2401, Japan  
Phone : 81-96-279-2985 Fax : 81-96-279-2986

# HORIBA World-Wide Network

## BRAZIL

### HORIBA Instruments Brasil, Ltda.

Rua Presbítero Plínio Alves de Souza, 645,  
Loteamento Multivias, Jardim Ermida II - Jundiá São  
Paulo - CEP 13.212-181 Brazil  
Phone : (55)-11-2923-5400 Fax : (55)-11-2923-5490

### TCA/HORIBA Sistemas de Testes Automotivos Ltda.

Avenida Luigi Papaiz, 239 - Campanário, Diadema,  
São Paulo, Brazil CEP: 09931-610  
Phone : (55)-11-4224-0200 Fax : (55)-11-4227-3133

## CANADA

### HORIBA Canada, Inc.

Unit102, 5555 North Service Road Burlington,  
Ontario, Canada, L7L 5H7  
Phone : (1)-905-335-0234 Fax : (1)-905-331-2362  
**London Office**

347 Consortium Court, London, Ontario, Canada,  
N6E 2S8  
Phone : (1)-519-668-6920 Fax : (1)-519-668-8437  
**Mississauga Office**

5700 Timberlea Blvd., Suite 2, Mississauga,  
Ontario, L4W 5B9 CANADA  
Phone : (1)-905-629-8066

## U.S.A.

### HORIBA Americas Holding Incorporated

9755 Research Drive, Irvine, CA 92618, U.S.A.  
Phone : (1)-949-250-4811

### HORIBA Instruments Incorporated

9755 Research Drive, Irvine, CA 92618, U.S.A.  
Phone : (1)-949-250-4811 Fax : (1)-949-250-0924  
**Ann Arbor Office**

5900 Hines Drive, Ann Arbor, MI 48108, U.S.A.  
Phone : (1)-734-213-6555 Fax : (1)-734-213-6525  
**Austin Office**

9701 Dessau Road, Suite 605, Austin, TX 78754,  
U.S.A.  
Phone : (1)-512-836-9560 Fax : (1)-512-836-8054  
**Canton Office**

5449 Research Drive Canton, MI 48188, U.S.A.  
Phone : (1)-800-445-9853 Fax : (1)-734-483-1592  
**Chicago, IL Field Office**

554 Anderson Drive, Unit A Romeoville, IL 60446,  
U.S.A.  
Phone : (1)-815-372-9076  
**Fletcher Office**

270 Rutledge Road, Unit D Fletcher, NC 28732, U.S.A.  
Phone : 1-828-676-2801 Fax : 1-828-676-2805  
**Houston Office**

5390 Bay Oaks Drive, Pasadena, TX 77505  
Phone : 1-281-482-4334 Fax : 1-281-674-6058  
**Novato Field Office**

359 Bel Marin Keys Blvd, #18, Novato, CA 94949  
**HORIBA New Jersey Optical Spectroscopy Center**  
20 Knightsbridge Rd, Piscataway, NJ 08854, U.S.A.  
Phone : (1)-732-494-8660 Fax : (1)-732-549-5125  
**Portland Office**

7007 S.W. Cardinal Lane, Suite 185, Portland, OR  
97224, U.S.A.  
Phone : (1)-503-624-9767 Fax : (1)-503-968-3236  
**HORIBA Reno Technology Center**

3740 Barron way Reno, Nevada 89511, U.S.A.  
Phone : (1)-775-358-2332 Fax : (1)-775-358-0434  
**Sunnyvale Office**

430 Indio Way, Sunnyvale CA 94085, U.S.A.  
Phone : (1)-408-730-4772 Fax : (1)-408-730-8975  
**Troy Office**

2890 John R Road, Troy, MI 48083, U.S.A.  
Phone : (1)-248-689-9000 Fax : (1)-248-689-8578

## AUSTRIA

### HORIBA (Austria) GmbH

Kaplanstrasse 5, A-3430 Tulln, Austria  
Phone : (43)-2272-65225 Fax : (43)-2272-65225-45

## BELGIUM

### HORIBA Europe GmbH, Antwerp Branch

Duwijkstraat 17, 2500 Lier, Belgium  
Phone : (32)3 281 57 92 Fax : (32)3 230 06 95

## CZECH

### HORIBA Czech Olomouc Factory

Zeleznicni 512/7, 772 00 Olomouc, Czech Republic  
Phone : (420) 588 118 365 Phone : (420) 588 118 393  
**HORIBA Czech Prague Office**

Prumyslova 1306/7, CZ-10200, Praha 10, Czech  
Republic  
Phone : (420) 246 039 265

## FRANCE

### HORIBA Europe Holding SASU

14 Boulevard Thomas Gobert - CS 45002 - 91120  
PPalaiseau - France

### HORIBA Europe Research Center

14 Boulevard Thomas Gobert - Passage Jobin Yvon  
CS 45002 - 91120 Palaiseau - France  
Phone : (33)-1-69-74-72-00 Fax : (33)-1-69-31-32-20

**HORIBA FRANCE SAS, Longjumeau Office**  
16-18, rue du Canal, 91165 Longjumeau Cedex,  
France  
Phone : (33)-1-69-74-72-00 Fax : (33)-1-69-09-07-21

**HORIBA FRANCE SAS, Lille Office**  
455 avenue Eugène Avinée - 59120 LOOS - France  
Phone : (33)-1-69-74-72-00 Fax : (33)-3-20-59-18-08

### HORIBA ABX SAS

Parc Euromédecine, rue du Caducée, BP7290, 34184  
Montpellier Cedex 4, France  
Phone : (33)-4- 67-14-15-16 Fax : (33)- 4-67-14-15-17

## GERMANY

### HORIBA Europe GmbH / Oberursel Office

Hans-Mess-Str.6, D-61440 Oberursel, Germany  
Phone : (49)-6172-1396-0 Fax : (49)-6172-1373-85  
**HORIBA Europe GmbH, Darmstadt Office**

Landwehrstrasse 55, D-64293, Darmstadt,  
Germany  
Phone : (49)-6151-5000-0 Fax : (49)-6151-5000-3865  
**HORIBA Europe GmbH, Dresden Office**

Hugo-Junkers-Ring 1, 01109 Dresden, Germany  
Phone : (49)-351-8896807 Fax : (49)-351-8896808  
**HORIBA Europe GmbH, Florsheim Office**

Mariechen-Graulich-Straße 10-12a, 65439 Flörsheim,  
Germany  
Phone : 49 6145 37699-12

**HORIBA Europe GmbH, Hanover Office**  
Frankenring 14, D-30855 Langenhagen, Germany  
Phone : (49)-511-65523987 Fax : (49)- 511-54571751  
**HORIBA Europe GmbH, Korschbroich Office**

Friedrich-Ebert-Str. 9-11, D-41352 Korschbroich,  
Germany  
Phone : (49)-2161-47537-0  
**HORIBA Europe GmbH, Leichlingen Office**

Julius-Kronenberg-Str. 9, D-42799 Leichlingen,  
Germany  
Phone : (49)-2175-8978-0 Fax : (49)-2175-897850  
**HORIBA Europe GmbH, Munich Office**

Waldmeisterstr. 72-74/Robinienstr. 66, D-80935  
Munich, Germany  
Phone : (49)-89-2444779-0 Fax : (49)-89-2444779-10  
**HORIBA Europe GmbH, Potsdam Office**

Dennis-Gabor-Str. 2, D-14469 Potsdam, Germany  
Phone : (49)-3316-4900-70 Fax : (49)-3316-4900-74  
**HORIBA Europe GmbH, Stuttgart Office (Boeblingen)**

Hanns-Klemm-Str. 56, D-71034 Boeblingen,  
Germany  
Phone : (49)-7031-677-9440 Fax : (49)-7031-677-9450  
**HORIBA Europe GmbH, Stuttgart Office (Neuhausen)**

Zabergaeustr. 3, D-73765 Neuhausen, Germany  
Phone : (49)-7158-933-800 Fax : (49)-7158-933-899  
**HORIBA Europe GmbH, Wolfsburg Office**

Klauskamp, Heinenkap II 38444 Wolfsburg ,  
Germany  
Phone : (49)-5361-38653-16 Fax : (49)-5361-38653-24

**HORIBA Jobin Yvon GmbH**  
Neuhofstrasse 9, D\_64625, Bensheim, Germany  
Phone : 49(0)62-51-84-750 Fax : 49(0)62-51-84-7520

**HORIBA FuelCon GmbH**  
Otto-von-Guericke-Allee 20, 39179 Barleben, Germany  
Phone : 49 39203 514 400 Fax : 49 39203 514 409

**HORIBA Tocadero GmbH**  
Johann-Hittorf-Str. 8 12489 Berlin Germany  
Phone : 49 (0)30 6392 3150 Fax : 49 (0)30 6392 3151

**BeXema GmbH**  
Steinfeldstraße 2a, 39179 Barleben, Germany  
Phone : 49 39203 514 200 Fax : 49 39203 514 209

## ITALY

### HORIBA ITALIA Srl

Via Luca Gaurico 209 - 00143 ROMA, Italy  
Phone : (39)-6-51-59-22-1 Fax : (39)-6-51-96-43-34  
**HORIBA ITALIA SRL, Torino Office**

Via Feroggio, 30, 10151 Torino, Italy  
Phone : (39)-1-19-04-06-01 Fax : (39)-1-19-00-04-48  
**HORIBA ABX SAS, Italy Branch**

Viale Luca Gaurico 209/211, 00143 Roma, Italy  
Phone : (39)-6-51-59-22-1 Fax : (39)-6-51-96-43-34

## NETHERLANDS

### HORIBA Europe GmbH, Netherlands Branch

Science Park Eindhoven 5080 (Industrial park  
"Ekkersrijt") 5692 EA, Son, Netherlands  
Phone : (31)-40-2900240 Fax : (31)-40-2900624

## POLAND

### HORIBA ABX Sp. z o.o.

Aleja Niepodleglosci 18  
02-653 Warszawa (Warsaw), Poland.  
Phone : (48)-22-673-2022 Fax : (48)-22-673-2026

## PORTUGAL

### HORIBA ABX SAS, Portugal Branch

Alfrapark - Estrada de Alfragide n° 67, Edificio F -  
Piso 0 Sul, 2610-008 Amadora, Portugal  
Phone : (35)-12-14-72-17-70 Fax : (35)-12-14-72-17-89

## ROMANIA

### HORIBA (Austria) GmbH, Romania Branch

B-dul.Republicii, nr. 164, Etaj Parter, Birourile nr. 3 si  
4, Pitesti, 110177, Judetul Arges, ROMANIA  
Phone : (40)-348-807117 Fax : (40)-348-807118

## RUSSIA

### HORIBA OOO

Altufievskoe shosse, 13, building 5, 127106, Moscow,  
Russia  
Phone : (7)-495-221-87-71 Fax : (7)-495-221-87-68  
**HORIBA OOO, Zelenograd Office**

Office 106, 2nd West st., 1, build 1, 124460,  
Zelenograd city, Moscow, Russia  
(\*Phone : 7)-499-995-09-54

## SPAIN

### HORIBA ABX SAS, Spain Branch

Calle Apolonio Morales. Num. 6 (Bajos), 28036 Madrid,  
Spain  
Phone : (34)-91-353-30-10 Fax : (34)-91-353-30-11  
**HORIBA MIRA SPAIN, S.L.**

Calle Oficios, nave 22, 04620 Vera (Almería)  
Phone : (34)-950-39-11-53

## SWEDEN

### HORIBA Europe GmbH, Sweden Branch (Gothenburg)

Grimboasen 10 A, S-417 05 Gothenburg, Sweden  
Phone : (46)-10-161 1500 Fax : (46)-10-161 1503  
**HORIBA Europe GmbH, Sweden Branch (Sodertalje)**

Sydhamnsvagen 55-57, SE- 15138, Sodertalje, Sweden  
Phone : (46)-8-550-80701 Fax : (46)-8-550-80567

## TURKEY

### HORIBA Europe GmbH, Istanbul Office

Veysel Karani Mahallesi, Colakoglu Sokak No: 10,  
Rings Rezidans D:23, PK: 34885, Sancaktepe /  
Istanbul, Turkey  
Phone : 90 216 572 1166 Fax : 90 216 572 1167

# HORIBA World-Wide Network

## UNITED KINGDOM

### HORIBA UK Limited

Kyoto Close Moulton Park Northampton NN3 6FL  
United Kingdom  
Phone : 44 (0)1604 542500 Fax : 44 (0)1604 542699

### HORIBA UK Finance Limited

Kyoto Close Moulton Park Northampton NN3 6FL  
United Kingdom  
Phone : 44 (0)1604 542500

### HORIBA Jobin Yvon IBH Ltd.

133 Finnieston St. Glasgow G3 8HB, United Kingdom  
Phone : (44)-141-229-67-89 Fax : (44)-141-229-67-90

### HORIBA Test Automation Limited

Brook Court Whittington Hall Worcester WR5 2RX,  
United Kingdom  
Phone : (44)-1905-359359 Fax : (44)-1905 359332

### Old HORIBA MIRA Certification Limited

Watling Street, Nuneaton, Warwickshire, CV10 0TU,  
United Kingdom  
Phone : (44)-24-7635-5000

### HORIBA MIRA Limited

Watling Street, Nuneaton, Warwickshire, CV10 0TU,  
United Kingdom  
Phone : (44)-24-7635-5000  
**HORIBA MIRA Limited, Quatro Park**  
Unit 1, Quatro Park, Paycocke Road, Basildon,  
Essex, SS14 3GH, United Kingdom  
Phone : (44)-1268-290100

### HORIBA MIRA Certification Limited

Watling Street, Nuneaton, Warwickshire, CV10 0TU,  
United Kingdom  
Phone : (44)-24-7635-5000

### MIRA Land Limited

Watling Street, Nuneaton, Warwickshire, CV10 0TU,  
United Kingdom  
Phone : (44)-24-7635-5000

### MIRA Service Limited

Watling Street, Nuneaton, Warwickshire, CV10 0TU,  
United Kingdom  
Phone : (44)-24-7635-5000

### MIRA Technology Park Limited

Watling Street, Nuneaton, Warwickshire, CV10 0TU,  
United Kingdom  
Phone : (44)-24-7635-5000

## CHINA

### HORIBA INSTRUMENTS (SHANGHAI) CO., LTD

No.99, Chunxiu Rd, Anting Town, Jiading District,  
Shanghai, China 201804  
Phone : (86)-21-6952-2835 Fax : (86)-21-6952-2823

### HORIBA Technology (Suzhou) Co., LTD.

No.1 building, Industry park, No.101 Chenmenjing  
Rd, Taicang, Jiangsu, China (215400)  
Phone : (86)-0512-3306-6388

### HORIBA (China) Co., Ltd.

Room 1604, Building 1, No.185 Moyu Road, Anting  
Town, Jiading District, Shanghai, China, 201805  
Phone : (86)-21-6289-6060 Fax : (86)-21-6289-5553

### HORIBA (China) Trading Co., Ltd.

Unit D, 1F, Building A, Synnex International Park,  
1068 West Tianshan Road, 200335, Shanghai, China  
Phone : (86)-21-6289-6060 Fax : (86)-21-6289-5553

### HORIBA (China) Trading Co., Ltd., Beijing Branch

12F, Metropolis Tower, No.2, Haidian Dong 3 Street,  
Beijing, 100080, China  
Phone : (86)-10-8567-9966 Fax : (86)-10-8567-9066

### HORIBA (China) Trading Co., Ltd., Guangzhou Branch

Room 1611/1612, Goldlion Digital Network Center,  
138 Tiyy Road East, Guangzhou 510620, China  
Phone : (86)-20-3878-1883 Fax : (86)-20-3878-1810

### HORIBA Precision Instruments (Beijing) Co., Ltd.

Building1, No.3 yuan, Xixing Road, Houshayu Town,  
Shunyi District, Beijing, 101318 China  
Phone : 86-10 8492 9402 Fax : 86-10 8492 7216

### MIRA China Ltd.

Suite 501, Block B, Hongqiao Sunnyworld No. 1226  
South Shenbin Road Shanghai, 201106, China  
Phone : (86)-21-6220-6377 Fax : (86)-21-6220-6379

### MIRA China Ltd. Xiangyang Workshop

A27-1, Jiahai industrial park, High-tech District,  
Xiangyang, Hubei, 441004, China  
Phone : (86)-710-2578-268

## INDIA

### HORIBA India Private Limited

246, OKHLA INDUSTRIAL ESTATE, PHASE 3 NEW  
DELHI - 110020, India  
Phone : 91-11-4646-5000 Fax : 91-11-4646-5020

### HORIBA India Private Limited, Bangalore Office

No.55, 12th Main, Behind BDA Complex, 6th sector,  
HSR Layout, Bangalore South, Bangalore - 560102,  
INDIA  
Phone : (91)-80-4127-3637

### HORIBA India Private Limited, Chennai Office

No.9, 01 & 02 Floor, Ganapathy Colony, Thiru-Vi-Ka  
Industrial Estate, Guindy, Chennai , 600032 India  
Phone : (91)-44-42077899

### HORIBA India Private Limited, Haridwar Factory

Plot No. 26, Sector-7, IIE, SIDCUL, Haridwar,  
Uttarakhand - 249403, India  
Phone : (91)-1334-239139

### HORIBA India Private Limited, Kolkata Office

EK Tower/6th Floor/Office -4A, Action Area-II D,  
Newtown, Pin Code 700161, India  
Phone : (91)-90073-63356

### HORIBA India Private Limited, Technical Center

D-225, Chakan MIDC Phase-II, Bhamboli Village,  
Pune-410501, India  
Phone : (91) 21-3567-6000

### HORIBA India Private Limited, Nagpur Factory

Plot No B-3 & C-32 Butibori Phase 2, Industrial  
Area, Dist Nagpur, Nagpur, 441122, India  
Phone : (91) 71-0328-0200

## INDONESIA

### PT HORIBA Indonesia

Jl. Jalur Sutera Blok 20A, No. 16-17, Kel. Kunciran,  
Kec. Pinang Tangerang - 15144, Indonesia  
Phone : 62-21-3044 8525 Fax : 62-21-3044 8521

## KOREA

### HORIBA KOREA Ltd.

25, 94-Gil, Ijjik-Ro, Manan-Gu, Anyang-Si, Gyeonggi-  
Do, 13901, Korea  
Phone : (82)-31-296-7911 Fax : (82)-31-296-7913

### HORIBA KOREA Ltd., Ulsan Office

613, Doosan We've the Zenith, 1877, Sinjeong-  
Dong, Nam-Gu, Ulsan-Si, 44679, Korea  
Phone : (82)-52-275-0122 Fax : (82)-52-276-0136

### HORIBA MIRA Limited, Korea Branch Office

25, 94-Gil, Ijjik-Ro, Manan-Gu, Anyang-Si, Gyeonggi-  
Do, 13901, Korea  
Phone : (82)-70-4689-0680 Fax : (82)-31-296-7913

### HORIBA STEC KOREA, Ltd.

98, Digital valley-ro Suji-gu, Yongin-si Gyeonggi-do  
16878 Korea  
Phone : (82)-31-8025-6500 Fax : (82)-31-8025-6599

## PHILIPPINES

### HORIBA INSTRUMENTS (SINGAPORE) PTE LTD., MANILA OFFICE

27/F Tower 2 Enterprise Centre, 6766 Ayala Avenue  
cor Paseo de Roxas, Makati City, Philippines, 1226  
Phone : 63 2 8885 8468

## SINGAPORE

### HORIBA Instruments (Singapore) Pte Ltd.

3 Changi Business Park Vista #01-01, Singapore  
486051  
Phone : (65)-6-745-8300 Fax : (65)-6-745-8155

### HORIBA Instruments (Singapore) Pte Ltd., West Office

83 Science Park Drive, #02-02A, The Curie, Singapore  
118258  
Phone : (65)-6-908-9660

## TAIWAN

### HORIBA Taiwan, Inc.

8F.-8, No.38, Taiyuan St. Zhubei City, Hsinchu  
County 30265, Taiwan (R.O.C.)  
Phone : (886)-3-5600606 Fax : (886)-3-5600550

### HORIBA Taiwan, Inc. Tainan Office

1F., No.117, Chenggong Rd., Shanhu Township,  
Tainan County 741, Taiwan(R.O.C)  
Phone : (886)6-583-4592 Fax : (886)6-583-2409

## THAILAND

### HORIBA Holding (Thailand) Limited

46/8 Rungrojthanakul Bld., 1st , 2 nd Floor,  
Ratchadapisek Road., Huai Khwang Bangkok 10310,  
Thailand  
Phone : (66)-2-861-59-95 Fax : (66)-2-861-52-00

### HORIBA (Thailand) Limited

46/8 Rungrojthanakul Bld., 1st , 2 nd Floor,  
Ratchadapisek Road., Huai Khwang Bangkok 10310,  
Thailand  
Phone : 66 (0) 2 861 5995 ext.123 Fax : 66 (0) 2 861 5200

### HORIBA (Thailand) Limited East Office

46/8 Rungrojthanakul Bld., 1st , 2 nd Floor,  
Ratchadapisek Road., Huai Khwang Bangkok  
10310, Thailand  
Phone : 66 (0) 2 734 4434 Fax : 66 (0) 2 734 4438

## VIETNAM

### HORIBA Vietnam Company Limited

Lot 3 and 4, 16 Floor, Detech Tower II, No. 107  
Nguyen Phong Sac Street, Dich Vong Hau Ward,  
Cau Giay District, Hanoi, Vietnam  
Phone : (84)-24-3795-8552 Fax : (84)-24-3795-8553

### HORIBA Vietnam Company Limited, Ho Chi Minh Branch Office

The Office #01& 02, Level 23, AB Tower, 76A Le  
Lai, Ben Thanh Ward, District 1, Ho Chi Minh City  
Phone : 84 28 3829 9636 Fax : 84 28 3827 3068

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2, Miyano Higashi-cho, Kisshoin, Minami-ku, Kyoto 601-8510, Japan  
Phone : (81)75-313-8121  
E-mail : [readout@horiba.co.jp](mailto:readout@horiba.co.jp)  
URL : <https://www.horiba.com/publications/readout/>

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