

# Tailoring spectroscopic performance for high end material characterization by customizing grating based spectroscopic equipment

Harald Kroker<sup>1</sup> und Brice Villier<sup>2</sup>

<sup>1</sup> HORIBA Jobin Yvon GmbH,  
Hauptstr. 1, 82008 Unterhaching

<sup>2</sup> HORIBA Jobin Yvon S.A.S. ,

Avenue de la Vauve - Passage Jobin Yvon CS 45002 - 91120 Palaiseau - France

**Abstract** Typical spectroscopic equipment in research labs has varying levels of complexity, covering different applications. When going to industrial instrument design for material characterization, the demands become highly specific: Parameters like stray light performance, resolution, coverage, sensitivity, speed, size, robustness and cost need to be weighted against each other. Especially for large quantities, custom design is one way to target a key market with a unique instrument. This might involve design of a grating, tailoring to the optical configuration, proper detector choice and integration into the instrument. For higher level instrumentation, customization might be mandatory to enabling difficult application. Our approach will be illustrated by showing examples for different categories of spectroscopic equipment, to demonstrate the advantage of customization in fields like material characterization.

## 1 Introduction: Tailoring of Spectroscopic Equipment

There are very different types of spectroscopic equipment used in R&D or labs for material characterization, starting from simple mini spectrometers or photometers up to complex multi-million € research facilities. To show what tailoring and customization might enable, it makes sense to look into three different categories of instruments separately:

- Workhorse

This type of instrument is designed for a highly specific application, which are used for routine analysis of the same kind. It is operated by several users with little or no training. The goal is routine use in a highly efficient and simple way. For this instruments, it is important to "hide" technical details, and concentrate only on simple output results and their validity, e.g. "red or green" flag, even if the underlying technique might be complex. Typical examples are photometers, microplate readers, fluorimeters and Raman spectrometers.

- Advanced analytical tools

These enable a broader range of application. They are capable to solve some of the unexpected, new and exiting or more difficult analytical questions. Usually, these equipment is offered in a more modular, open way, e.g. with configurations optimized to the customer's demands. Upgrade options are important aspects for the selection of the right tool. To be able to achieve best results, more experienced and educated users are important who have to judge on the limits of the methods. (e.g. high end fluorimeters, advanced micro-Raman spectrometers, spectroscopic ellipsometers (SE))

- Unique research tool

This equipment makes use of state of the art techniques. Latest developments were incorporated to push the limits for detection and analytical capabilities. This type of instruments need full understanding of the techniques used. Checking for "features", errors and limits is a major part of data acquisition and analysis carried out by the user.

For new, demanding applications, it might happen, that the market doesn't offer well fitting solutions, or only very complex and expensive tools that are not really tailored to this new application.

We work on extending the capabilities of instruments in all of the three categories described above. This will be explained in some examples, split up into the three categories introduced above.

## 2 How to Help Making a Workhorse

### 2.1 Considerations for Workhorse Design

Common points for this type of equipment are:

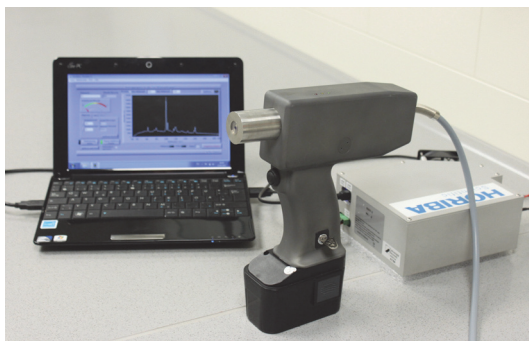
- simple operation
- robust performance
- high number quantities within a clearly defined target market
- moderate customer price
- "hidden" technique
- clear indication of the validity of result

To get a competitive instrument, these points need to be addressed. For typical spectroscopic techniques like photometry, absorption, fluorescence, Raman, NIR, emission, LIBBS or others, the demands differ a lot. Which means specifications and design parameters for the actual analytical method need to be carefully controlled, to reach a convincing performance level.

For a good instrument design, the crucial spectroscopic parameters which will determine the instrument's success (e.g. stray light, spectral resolution and range, sensitivity, speed, instrument size, environmental stability, and last but not least, cost) need to be identified, weighted for their relevance and carefully handled. Component selection has the ultimate goal to reduce the performance and cost to the necessary level. These instruments are usually built at significant number quantities, which means customization is a valuable method to control manufacturing costs.

Horiba as a grating manufacturer is active in this field as an OEM partner giving the opportunity to start customization at very basic components, like the grating, spectrometer and related optics hardware.

For this, we work very closely together with the equipment manufacturer, to find the optimum solution. One important point is to look for the value each partner can add to the project, and by this, define the best interface between the partners. Two examples can be presented to show how tailoring of spectroscopic equipment will lead to workhorse performance.



**Figure 23.1:** Mobile Raman setup, with “pistol” containing the Raman probe and the laser, the spectrometer and the control computer. (Picture courtesy of H.Schmidt)

## 2.2 Meat Qualification Using a Portable Raman Device

An optical method for analyzing raw meat non-invasively was developed to control different parameters that govern the quality of meat [1]. The device is able to measure parameters like freshness, meat type, pH, drip loss, shear force and others. These parameters can be attributed to detailed molecular components and their change with time after exsanguination [2]. Raman spectroscopy is known to provide a “fingerprint” of the molecular composition and structure of materials. It was selected as the appropriate analytical method, because it provides better correlation to classical, invasive reference methods than other optical techniques like fluorescence or VIS-NIR reflectance spectroscopy.

To achieve optimum results, it was mandatory to fine tune some key instrument parameters:

- **Laser wavelength:**  
It has to be reasonably short to get good detector sensitivity and high Raman efficiency, which is  $\sim \lambda^{-4}$ , but long enough to avoid excess fluorescent background.
- **Trade off between spectral resolution and coverage:**  
spectral lines need to be resolved, while sufficient range on the detector needs to be provided to measure all key lines.

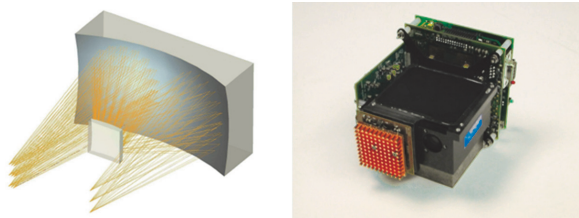
- High throughput and sensitivity:  
Integration time needs to be kept moderate, to avoid deep cooling of the detector.
- Mobility and robustness:  
The goal is a mobile instrument which is used in harsh environment (cooling rooms of abattoirs, at 100% humidity).

Taking this into account, Horiba provided a customized spectrometer system tailored to these demands. (See fig. 23.1) Recent publications are describing the method and results like aging of meat [1], pH of pork [3] or multiple parameters [2].

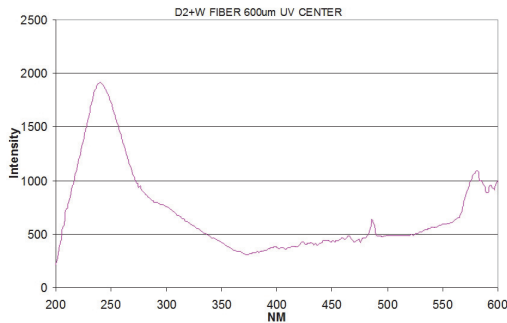
For getting results on the individual parameters, key features in the spectrum need to be separated and analyzed in detail. Here we show some steps necessary for estimating the pH values in meat (more details can be found in [3]):

- Getting Raman and reference data (puncture electrode) on different meat samples, 0.5h and 10h post mortem.
- Baseline correction (fluorescence background) by fitting a 5th order polynomial to the Raman spectra, followed by spectral smoothing.
- Intensity normalization.
- Generation of difference spectra, to investigate evolution with time of the Raman spectra.

Finally, the Raman-derived pH results were correlated with the reference measurement by different methods. Even the simplest method using the intensity ratio of only two spectral features gives strong correlation ( $R^2 = 0.71$ ). More robust predictions were achieved by applying more advanced regression methods. MLR (multiple linear regression), using the 11 peaks gives  $R^2$  of 0.78), while non linear methods (PLSR, partial least-square regression), which make use of the entire spectra, give an  $R^2 = 0.95$  and correlate very well even at low pH level. The apparent offset between Raman data and reference data is attributed to a dislocation of the actual measuring positions, reflecting a biological variance in the muscle.



**Figure 23.2:** Optical design of an all-reflective hyperspectral imager, and an example for a compact VIS imager including CCD



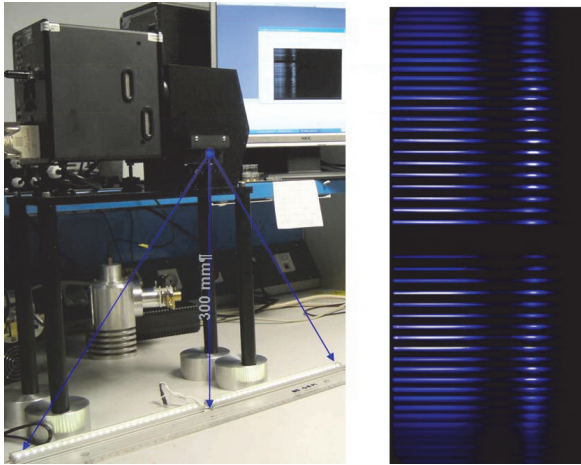
**Figure 23.3:** UV-VIS spectral output from combined D2 and halogen source

### 2.3 Hyperspectral Imager for UV Wavelengths

Hyperspectral imaging has his major roots in remote sensing, which is why it is carried out mainly in the atmospheric windows from VIS to MIR. This technique is becoming more important for material characterization in industrial environments, like waste sorting, food inspection and others, but is usually restricted to reflectivity measurements in the VIS-NIR range. Other techniques like fluorescence or Raman [4] are explored as next generation hyperspectral imaging, but don't seem to be very common up to know.

An example for a different spectral range is presented here:

We developed major hardware components for a UV hyperspectral imaging system: the imaging spectrograph and a dedicated relay optics system tailored to the special requirements of the UV wavelength.



**Figure 23.4:** Hyperspectral Imager for the UV. Left: Test setup with two LED arrays of 30cm length each. Right: Resolved raw spectra of individual LEDs

The UV CCD with  $512 \times 512$  p, was defined by the customer. The design goal was to record the UV reflectance spectra of samples running on a conveyor belt. The samples were illuminated by an UV line source of  $500 \times 2.5$  mm at a free distance of 300mm (see fig. 23.4).

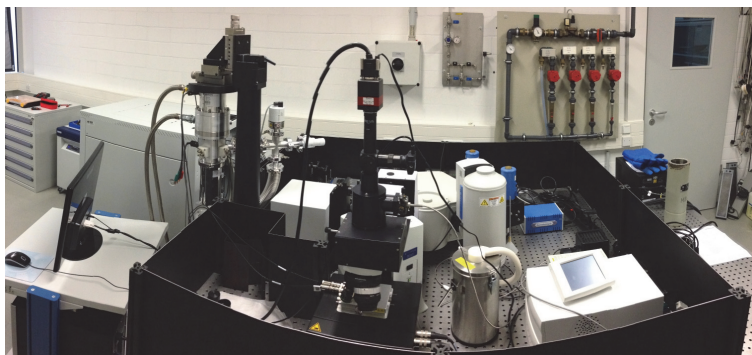
The main instrument challenges were:

- Spectral range: 200-500nm
- High sensitivity and throughput of the spectrometer: A F/3 design was achieved by using a convex holographic grating.
- Efficient relay optics with anamorphic magnification (1:50 and 1:25). Our 3 - mirror design matched performance specs very well.

Even though this spectrometer is designed for the UV, it will of course work for any other wavelength range with an appropriate grating.

### 3 How to Give More Flexibility to Advanced Instruments

Advanced research instruments were operated by highly skilled users, which often hold a PhD degree. This is the market of high level re-

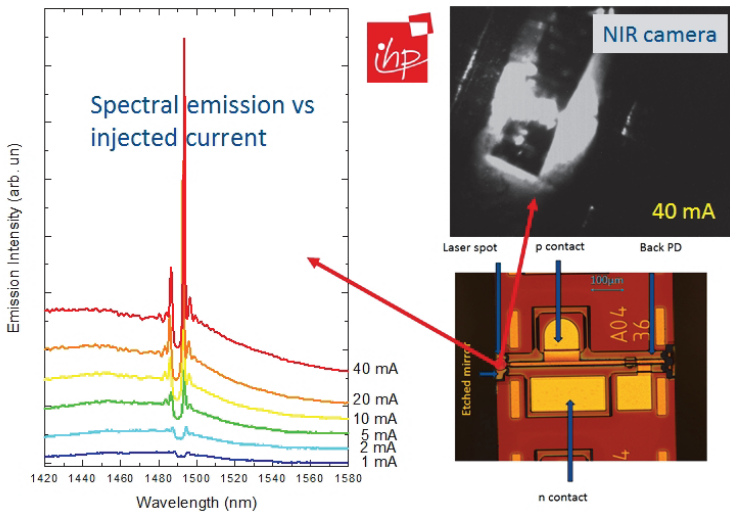


**Figure 23.5:** Overview on the IR-PL-EL instrument

tail instruments, that are offered by various vendors, including Horiba. But in material research, it is often hard to predict the future demands of the application, when new materials or combinations are developed. An important asset is to be able to enhance capabilities later, and is a major distinction to the workhorse instruments. Manufacturers take this into account and give some opportunity to upgrade the instrument by adding modules or advancing certain capabilities. This can be a further laser for a Raman tool, a life-time module upgrade in fluorescence, or a dedicated sw library to enhance data analysis functions. But tailoring goes one step further: the equipment's architecture is either open enough for customer extensions, or customized extensions, which means, either the researcher himself can include the needed capability, or the vendor does it.

An example is given here for a IR-Photo- and Electroluminescence instrumentation project, where it became quite clear from the beginning, that a retail instrument couldn't provide all the required measurement modes. The instrument was built by using modules and parts out of different categories:

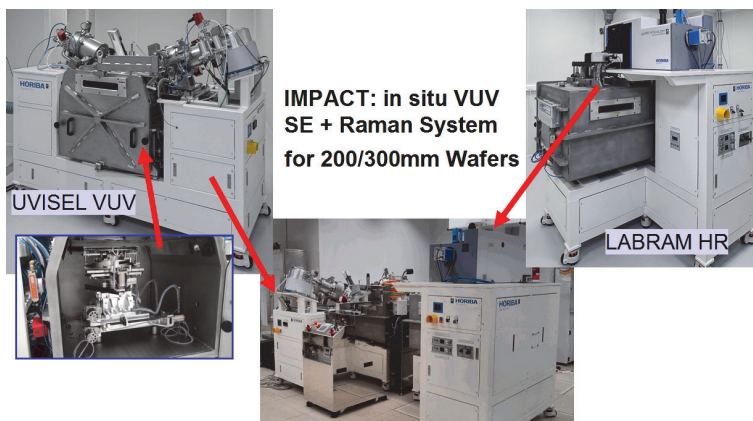
- Horiba standard spectroscopic components: iHR320 spectrograph; NIR array detector; IR single channel detectors (1-5 $\mu$ m)
- Special Horiba accessories: macro-PL interface; lens free microscope with free beam mirror coupling to spectrograph

**Results: laser emission from InP diodes (surface emitting laser)****Figure 23.6:** EL result for an InP surface emitting laser device

- Components from specially selected vendors: 10K macro cryostat; 77K micro cryostat; high power lasers; NIR-vision-camera; NIR/IR-objectives
- Customized components and design: confocal adaptation; extended IR range optics

Even though the tailoring was significant, only very moderate R&D effort was necessary, because most components had been developed already for other projects in the past, which means tailoring instrumentation by using "available" equipment and working experience can enable commercial solutions which were not available otherwise.

Some first results were shown in fig.23.6: The NIR emission from an vertical emitting laser is resolved both spectroscopically with the iHR320 and spatially with the NIR camera. The threshold current for lasing operation can be determined by looking at these signatures.



**Figure 23.7:** IMPACT hardware: main modules and assembly at customer site

## 4 How to Help Achieving Top End Instrumentation

For this category of instrumentation customization goes one major step further: we involve a dedicated R&D project team ("TIM") within our company to build unique instrumentation. Typical resources for this are:

- Standard and not-standard retail products from Horiba or other vendors
- Components/interfaces from customers: e.g. vacuum chambers, synchrotrons, ...
- Customized add-ons from Horiba's R&D project team: optics, mechanics, vacuum parts, electronics, sw, ...

A recent result is shown in fig. 23.7. This is an instrument that is built for the use at a high level research institute. The goal was to be able to measure different properties on large Si wafers without breaking the vacuum where the wafers are processed. Two main instruments were integrated into a cluster tool: An in-situ VUV spectroscopic ellipsometer (SE), and a micro Raman spectrometer. Even though we built VUV SE

working down to 150nm before using Horiba's VUV monochromators, this cannot be considered being a retail instrument. And it was further tailored to the needs of this special environment, which demanded significant R&D manpower.

For the Raman spectrometer, the main constituents of our retail instrument LabRam were used, but adapted for special demands like vacuum use. Further, a common vacuum environment including xyz tables and wafer handling was included, together with a sw interface to the customer's driving sw.

## References

1. H. Schmidt, K. Sowoidnich, M. Maiwald, B. Sumpf, and H. Kronfeldt, "Hand-held raman sensor head for in-situ characterization of meat quality applying a microsystem 671 nm diode laser," in *Advanced environmental, chemical, and biological sensing technologies VI*, 7312, *proceedings of SPIE*, 2009.
2. R. Scheier, A. Bauer, and H. Schmidt, "Early postmortem prediction of meat quality traits of porcine semimembranosus muscles using a portable raman system," in *Food and Bioprocess Technology*, 9 (2014), 2732-2741, 2014.
3. R. Scheier and H. Schmidt, "Measurement of the ph value in pork meat early postmortem by raman spectroscopy," in *Applied Physics B*, 111, 289-297, 2013.
4. M. DeBiasio, T. Arnold, G. McGunnigle, R. Leitner, D. Balthasar, and V. Rehrmann, "Detection of fire protection and mineral glasses in industrial recycling using raman mapping spectroscopy," in *Proc. SPIE 8032, Next-Generation Spectroscopic Technologies IV*, 80320H, May 2011.