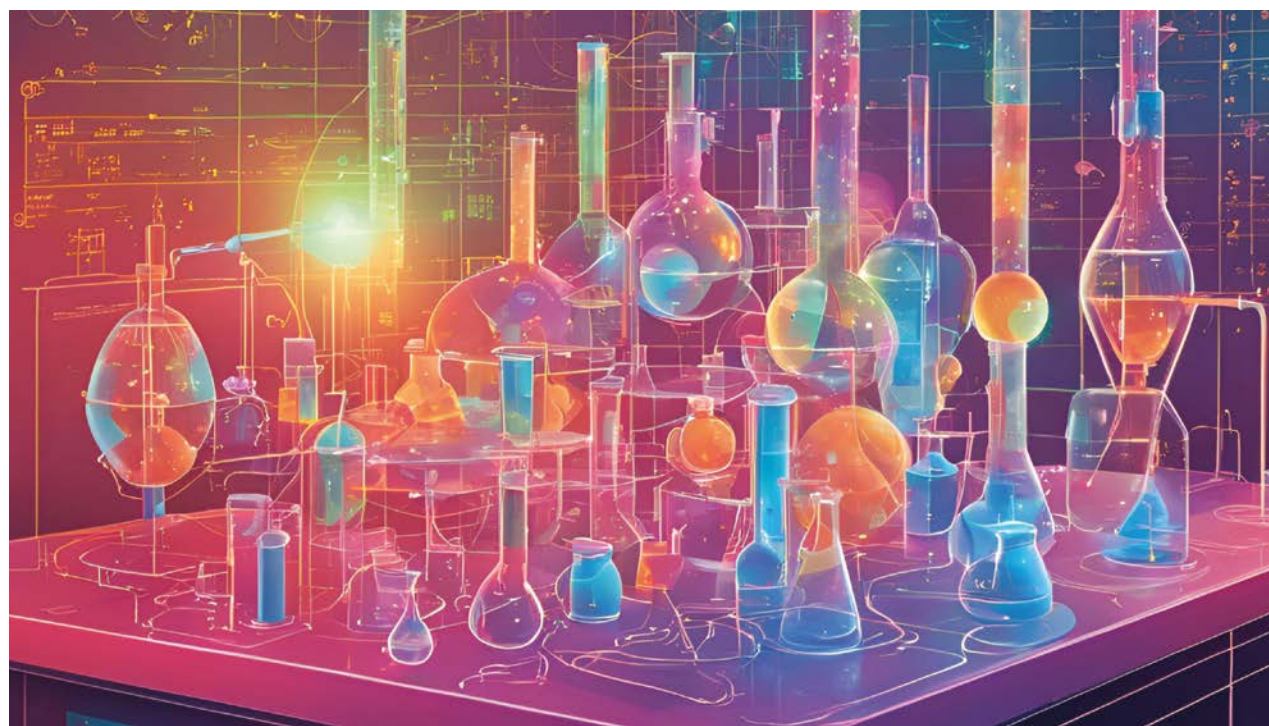


Addressing transferability and stability in Raman spectrometers

How to design instruments for industrial environments

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The invention of lasers has enabled the widespread use of Raman spectroscopy in scientific laboratories, and recently Raman spectroscopy has been applied in industrial environments as well. Based on Ibsen Photonics' experience as an OEM supplier of Raman spectrometers for various applications, this article reviews key concerns that must be addressed when designing a Raman spectrometer for industrial applications.

Raman spectroscopy was first demonstrated experimentally in 1928 by C. V. Raman and K. S. Krishnan. The technique relies on the inelastic scattering of monochromatic light in a sample and is often a complementary technique to infrared absorption spectroscopy.

In Raman scattering, an incident photon either gains or loses energy by interacting with intermolecular vibrations within a molecule. The change in energy corresponds to a blue or red shift in the wavenumber of the incident light. Because the vibrational modes of a molecule are unique to each molecule, the wavenumber shifts, i.e. the Raman spectrum constitutes a unique fingerprint for the molecule.

The invention of lasers in the 1960s enabled Raman spectroscopy to become a common tool in many scientific laboratories. During the past two decades, Raman spectroscopy has also found usage in more demanding industrial environments.

A Raman instrument typically consists of four fundamental subsystems: a laser, a probe, a spectrometer, and a software model, as shown in Fig. 1. The laser provides monochromatic light that illuminates the sample. The probe ensures that the laser light is focused on the sample and that the scattered light from the sample is collected and focused on the spectrometer. Generally, the probe includes delivery and collec-

tion optics, as well as several optical filters. The spectrometer detects the Raman spectrum, i.e. the light intensity versus wavenumber shift.

The scattered Raman light is usually weak and buried in background light. The software model must therefore include preprocessing to remove this background and any other undesired spectral artifacts. Differentiation between various molecular structures is often achieved through multivariate statistical data analyses – referred to as chemometrics models. These models correlate small differences in spectral features with differences in molecular structures.

A chemometrics model first involves calibration using a reference set of

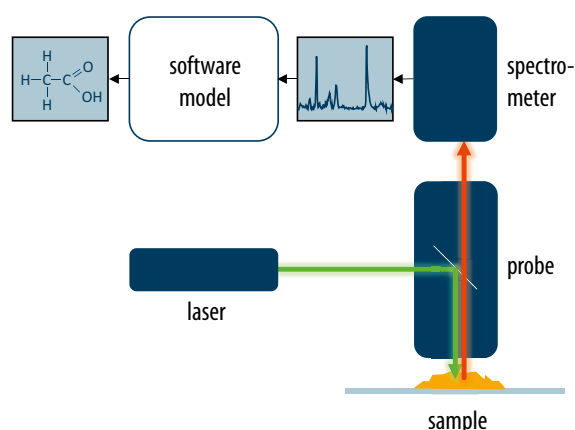


Fig. 1 Schematic view of a basic Raman system consisting of a laser, a probe, and a spectrometer

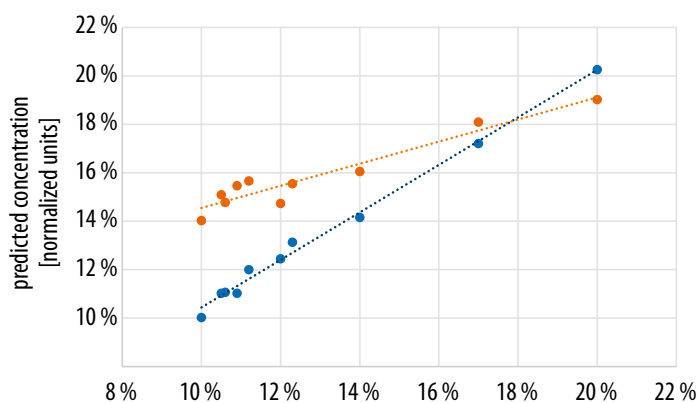


Fig. 2 Model predictions for two instruments versus measured concentrations. Blue marks: instrument providing acceptable results, orange: instrument providing incorrect results

samples with known concentrations, measured by a gravimetric method for instance. Then the model is used to predict the results for unknown samples. The better the original reference samples represent the variability of the unknown samples, the better the model predictions are.

Moving Raman spectroscopy out of the lab

A scientific laboratory often owns one or more highly advanced, general purpose Raman spectroscopy systems. The instruments are operated by skilled personnel, and software models are developed and refined by scientific experts. However, the operating conditions change when a Raman spectroscopy system is to be used in an industrial environment such as on the factory floor.

First of all, the instruments are often purpose-made to measure only a few well-known types of samples. An exam-

ple of an application would be the outgoing quality check of the amount of active ingredients in pharmaceutical tablets. The instruments could be operated close to 24/7 by non-experts and just have a simple and intuitive interface and a minimal amount of daily calibration.

Industrial Raman instruments can also be exposed to harsh environmental conditions such as temperature variations and vibrations. It is therefore important that the instruments are designed to be robust against such environmental conditions.

In contrast to the situation in a scientific laboratory, it is common that many identical instruments are used on the various production lines and/or factory sites. Also, the instruments must be easily replaceable for maintenance and repairs.

Transferability

As mentioned earlier, the interpretation of measured raw Raman spectra

often requires chemometrics models. Model transferability means that the same result – within acceptable limits – is obtained when the same sample is measured with different Raman instruments. Since industrial applications of Raman spectroscopy involve the same measurement by many similar instruments that all operate with the same global chemometric model, transferability becomes hugely important.

Ideally, the Raman systems should all be identical, but there will inevitably be slight variability between the individual instruments due to small differences in the parts used. Another contributing factor to variability is the operating conditions of the instruments. These variations can be accounted for during model calibration to some extent, but to account for all possible variations would require an impractically large set of reference Raman systems and operating conditions. Typically, five to

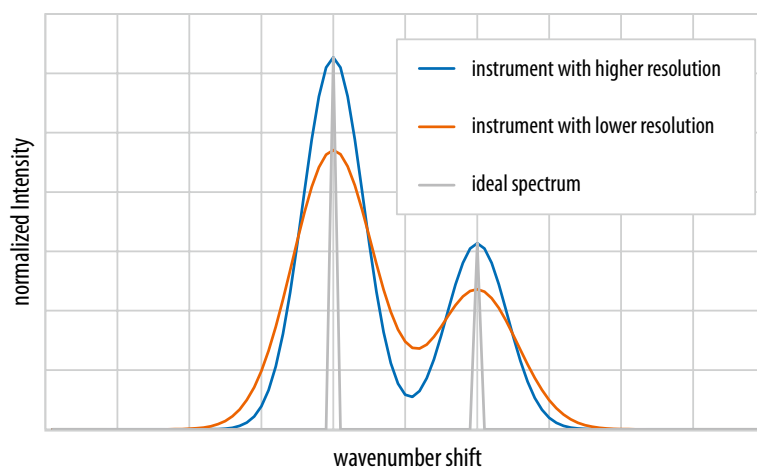


Fig. 3 Simplified Raman spectra illustrating the effect of finite resolution of the instrument

Company

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Ibsen Photonics provides leading industrial companies with best-in-class gratings and spectrometers, accelerating their growth in existing and emerging markets. Our compact, high-performance spectrometers boast minimal unit-to-unit performance variation and robust environmental stability, leading to reduced implementation costs and eliminating the need for field calibration and recalibration. We serve as a strong long-term strategic partner for industrial companies, delivering customized solutions tailored to their specific needs.

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ten reference instruments are used to build a chemometrics model.

Wavenumber calibration, spectral resolution, intensity calibration, and photometric linearity are all instrument parameters that can influence the transferability of a chemometric model. Fig. 2 shows an example of sample concentration measured with two different Raman instruments. The x-axis represents the true concentration of the reference samples measured by a gravimetric method. The blue marks are predictions based on an instrument sufficiently similar to the reference instruments used for building the model, with the results in line with the measured values. The orange marks, however, are predictions made using an instrument substantially different from the reference instruments, predicting significantly incorrect results.

Spectrometer resolution

Let us examine one of the key parameters influencing model transferability: spectrometer resolution. Raman spectroscopy generally requires high-resolution spectrometers to resolve closely spaced peaks. Resolution is therefore a particularly important parameter for Raman spectrometers.

Fig. 3 shows a simplified plot of an ideal Raman spectrum with two peaks measured using two different instruments. One instrument has a higher resolution, while the other has a lower resolution. The effect of finite spectrometer resolution is that the peaks are broadened. The poorer the resolution, the wider the peaks, and the lower each peak.

The diagram clearly illustrates how resolution influences the overall shape of the spectrum. Furthermore, Fig. 3 shows resolution peaks for a spectro-

meter with symmetrical resolution peaks. However, it is not uncommon for the resolution peaks to be asymmetric. If the asymmetry varies from instrument to instrument, it can pose a further challenge for the chemometrics model to correctly interpret the spectrum.

How to control instrument variability

Instrument variability arises from the combined effect of many small variations in the components used to build the spectrometer. These variations stem from the tolerance specifications of the components. The tighter the tolerances, the higher the cost, so tolerances should always be balanced against the overall cost target of the Raman spectrometer. For example, the resolution of a spectrometer is influenced by the tolerances in the focal lengths of lenses and optomechanical mounts as well as mounting tolerances during assembly. To achieve model transferability in volume production, it is crucial that the spectrometers are sufficiently similar. First and foremost, the key to this is designing the spectrometer to be as insensitive as possible to variations in its components and assembly methods. Secondly, precise alignment of each spectrometer during manufacture can maintain parameters such as resolution and peak asymmetry within certain limits. Alignment involves adjusting the position of components such as lenses while monitoring an instrument parameter – like resolution and peak asymmetry – to compensate for unit-to-unit variations.

A good spectrometer design therefore requires an in-depth tolerance analysis of the entire system to identify the components that influence instrument variability the most. Com-

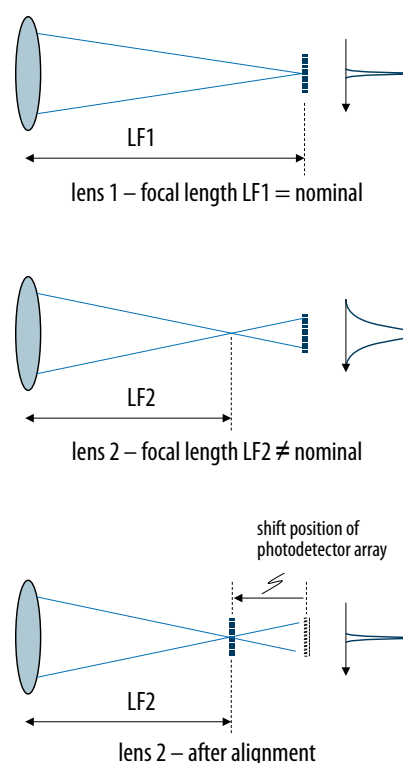


Fig. 4 Illustration of how differences in focal length between different lenses can be compensated by adjusting the position of the photodetector array

pensating alignment methods should be built into the design based on the outcome of the tolerance analysis. This process requires a deep understanding of the nature of volume production of optomechanical subsystems to ensure a good design for manufacture. Fig. 4 schematically illustrates a simplified example of alignment to achieve the same resolution for two instruments. The top drawing in Fig. 4 shows a situation where the lens used has the nominal focal length, which is the focal length for which the instrument was designed. The middle and lower draw-

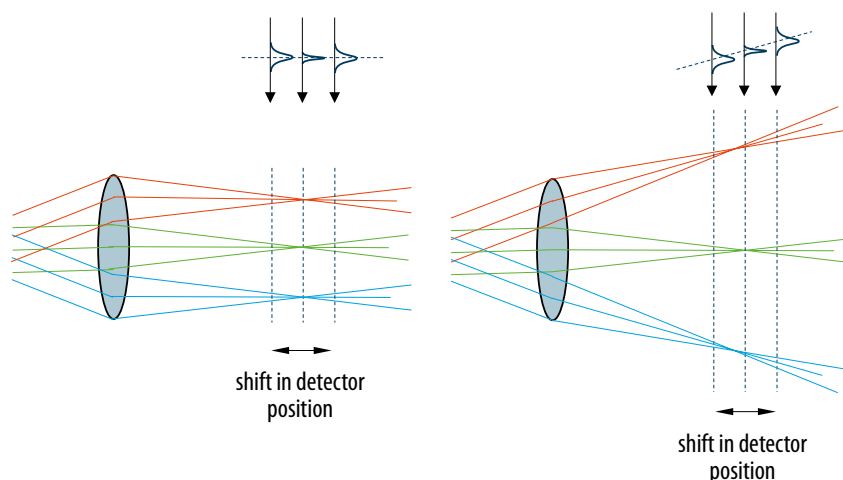


Fig. 5 Center wavelength shift sensitivity of the design: (l) telecentric design with no change in center wavelength due to detector displacement; (r) non-telecentric design with center wavelength changes due to detector displacement

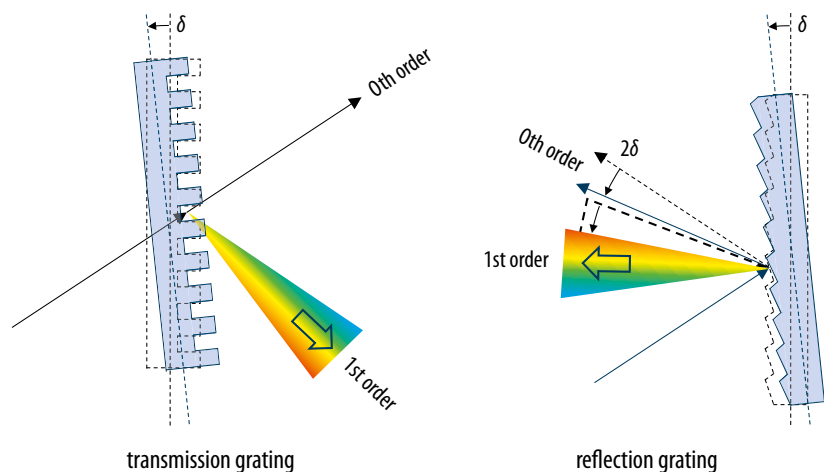


Fig. 6 Illustration of sensitivity to angular displacement of diffraction gratings: (l) transmission grating is not sensitive to small angular displacements; (r) reflection grating is sensitive to angular displacement

ings in Fig. 4 depict a situation where the focal length of the lens is too short, causing the beam to be out of focus on the photodetector array. By moving the photodetector array to the focal point of this lens, the resolution is restored to the desired narrow tolerance.

Environmental stability

Instruments used in industrial settings can be exposed to a range of environmental influences that are not present in a laboratory. For example, the ambient temperature and humidity may vary due to changes in weather conditions or the presence of nearby machinery generating heat and/or moisture. Additionally, if the instrument is mounted on another machine it may experience vibrations from that machine.

Variations in the ambient environment can have detrimental effects on Raman instruments. The different components of the instrument are made from various materials, such as glass, polymers, and metals. These materials expand and contract differently with temperature changes, which can lead to performance degradation of the spectrometer or even permanent damage to

the instrument. Similarly, vibrations may cause components inside the spectrometer to shift positions, resulting in performance degradation. In the worst case, a component such as a lens might completely detach from its mount, rendering the device inoperative.

How to control instrument stability

The key to maintaining instrument stability is to design it to be as insensitive and robust as possible against environmental influences. In general, it is preferable to design the spectrometer without any moving parts, such as rotating diffraction gratings or adjustable slits. This is because motor-driven components wear out over time and are susceptible to vibrations. For this reason, fixed-grating, diode array-based Raman spectrometers are preferred over those based on scanning gratings.

The optical design of a spectrometer can significantly influence its sensitivity to temperature variations. For instance, the distance between the last lens in the spectrometer and the photodetector array may change due to thermally induced expansion and

contraction of the metal mounts. Fig. 5 depicts two different design options: a telecentric and a non-telecentric design. In the telecentric design, the shift in detector position does not alter the focal point position on the detector array but does broaden the resolution peak. The focal point corresponds to the center wavelength of a peak measured by the spectrometer. In contrast, in a non-telecentric design, the shift in detector position leads to a shift in the focal point position and, consequently, the center wavelength. Additionally, the shift in center wavelength varies for different parts of the spectrum.

Another aspect of the optical design that can influence the sensitivity to component displacement is the choice of transmissive rather than reflective optics. Fig. 6 illustrates an example of this, namely the angular sensitivity of a reflection grating versus a transmission grating. An angular rotation can be the result of vibration or another asymmetric mechanical disturbance on the grating mount. The reflective grating acts like a mirror, which means that an angular rotation of one degree results in an angular shift of the dif-

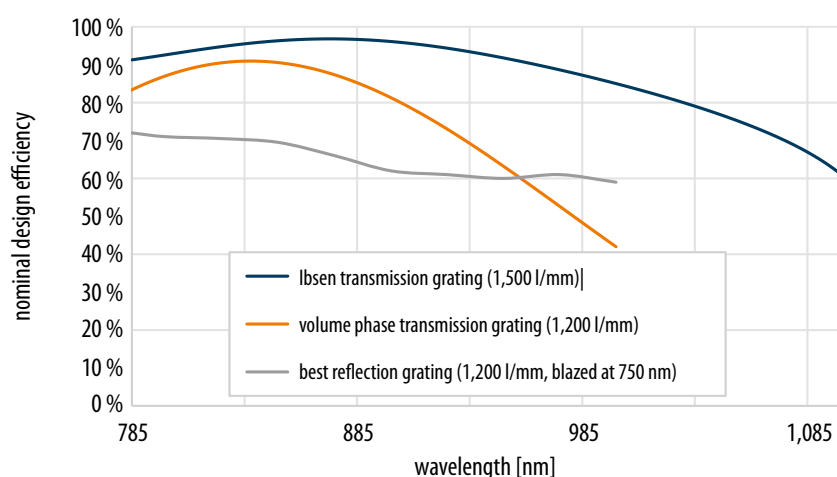


Fig. 6 Comparison of diffraction efficiency for typical diffraction gratings

fracted grating orders by two degrees. The consequence is that the spectrum shifts on the detector array. In contrast, the grating orders of a transmission grating do not rotate with small angular rotations of the grating. This exemplifies why transmission optics are less sensitive to rotational changes than reflection optics.

High-resolution, compact Raman spectrometers typically require gratings with a high groove density and diffraction efficiency as close to 100 % as possible. Transmission gratings with a high groove density can offer nearly 100 % polarization-insensitive diffraction efficiency. In contrast, blazed reflection gratings with high groove densities generally provide an average polarization-dependent efficiency of around 60 %. See Fig. 7 for a comparison of typical gratings used for a 785 nm laser Raman spectrometer. This throughput advantage further highlights the benefit of using transmission gratings over reflection gratings.

Summary

As Raman spectroscopic instruments find use in industrial settings, instrument-to-instrument transferability and robustness against external environmental influences become critical. Although chemometric models can correct for some level of instrument variability, it is still important to maintain certain instrument characteristics, such as peak resolution, within specific boundaries. This can be achieved by carefully designing the spectrometer and using assembly methods based on a comprehensive tolerance analysis. Furthermore, active alignment of each instrument is essential to obtain minimal unit-to-unit variation.

Environmental factors like temperature changes and vibration can degrade the performance of a Raman spectrometer. To reduce its sensitivity to such external disturbances, the spectrometer should be designed with no moving parts and a tolerance for component displacements. Furthermore, the use of transmission optics rather than reflective optics helps to improve overall throughput and reduce sensitivity to environmentally induced displacements.

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