Raman spectroscopy to support REACH registration of gases

Key Issues

- Compliance with EU REACH legislation
- Simple analysis of many gas-phase species including homonuclear diatomics
- Complementary information with other common methods of gas analysis

Introduction

REACH is a European Union regulation concerning the Registration, Evaluation, Authorisation, and Restriction of Chemicals.[1] It came into force in June 2007 with the aim of ensuring a high level of protection of human health and the environment from the use of chemicals, and to make manufacturers and importers of chemicals responsible for understanding and managing the risks associated with their use.

Under REACH, manufacturers or importers must register substances with the European Chemicals Agency (ECHA), a process that requires a comprehensive set of analytical data in order to verify the identity of the material. Typically, the ECHA requires a bare minimum of UV-VIS, FTIR, and NMR or mass spectrometry to confirm molecular structures, as well as GC or LC to assess impurities. In some cases, additional or alternative techniques such as X-ray diffraction or X-ray fluorescence may be required.

While it is straightforward, at least in principle, to find enough techniques to characterize solids and liquids to meet the requirements of ECHA, gases present more of a problem since many of the techniques mentioned above are not very useful for gases. While GC, mass spectrometry, and FTIR provide very useful information, NMR spectroscopy of gases is not commonplace, and UV-VIS provides limited information unless the gases contain strong chromophores. There is a widespread concern that ECHA may reject applications supported by just three analytical techniques, so there is a real need for other approaches for characterizing gases. Raman spectroscopy has a lot to offer in this respect, because it allows observation of homonuclear diatomics, which are infrared inactive, as well as providing similar but complementary information to FTIR spectroscopy, which is an accepted tool for REACH registration.

Raman measurement of gases

Raman scattering from gases or vapors at atmospheric pressure is generally weak because of the low number density of molecules in the sample. However, a Raman probe enables high-quality data to be obtained from gases on a short timescale. In this work, a Raman probe was connected to a Raman analyzer fitted with a 100-mW 532-nm diode-pumped Nd:YAG laser and a Peltier-cooled CCD detector. Figure 1 shows the sample-handling system used in this work. The Raman analysis was carried out *in situ* with the cell in the gas handling line.

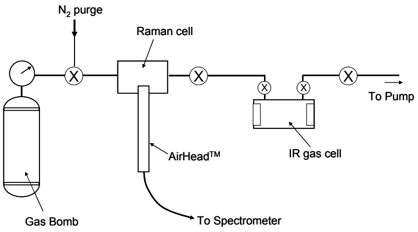

Figure 1: Schematic diagram of gas-handling system.

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

Example: CH_4 / H_2 mixture

Figure 2 shows the spectrum obtained from a sample of methane containing ~1% hydrogen. The strong, sharp rovibrational band patterns near 3000 and 1500 cm^{-1} are a highly characteristic fingerprint for methane gas.[2] The single band near 4159 cm^{-1} is the H_2 stretching vibration. This mode is inactive in the infrared spectrum due to the lack of a change in the H_2 dipole moment during the vibration. In this case, FTIR spectroscopy (the default ECHA-requested technique for vibrational spectroscopy) would easily detect methane, but it would give a misleading picture of the material composition, since it cannot detect the hydrogen component. As well as the H_2 stretching band, a series of sharp bands appears between 1040 cm^{-1} and 350 cm^{-1}. These are pure rotational transitions of the H_2 molecule.[3] (These transitions occur at higher wavenumber than for other species because H_2 has a very low moment of inertia.) Their distinctive pattern and intrinsic strength make it trivial to detect H_2 at just 1% concentration in CH_4. Thus, a significant deficiency in current analytical technologies (a need for gas-phase-capable technology for quantitative measurement of homonuclear diatomics) can be overcome by using Raman spectroscopy.

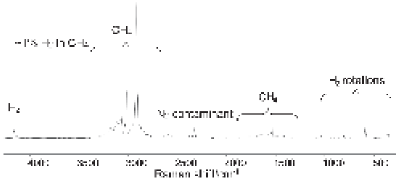

Figure 2: Raman spectrum of 1% H_2 in CH_4. The sharp bands below 1040 cm^{-1} are the pure rotational transitions of the H_2 molecule.

Example: isobutylene and butadiene

Figure 3 shows the Raman spectra of two samples of unsaturated C_4 gases, obtained by averaging six scans of 30 seconds duration. The spectrum of the first sample (upper trace, blue) is consistent with isobutylene. The lower trace shows that the second sample is predominantly butadiene,[2] but several additional weak bands (marked with vertical arrows) confirm the presence of isobutylene as a minor component.

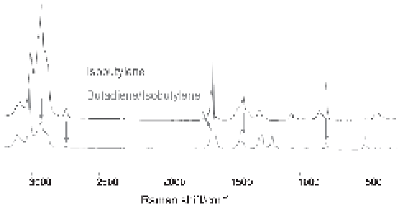

Figure 3: Raman spectra of C_4 gases. The upper trace is consistent with isobutylene; the lower trace has strong bands due to butadiene and several weaker bands (arrowed) due to isobutylene.

Other gases

Finally, to illustrate the general utility of the Raman probe for analyzing simple gases, Figure 4 shows spectra of three other hydrocarbon samples. Each spectrum was obtained by averaging six scans of 30 seconds duration. The upper and middle traces are consistent with n-butane and propane, while the sample in the lower trace is predominantly propene, with a minor propane impurity.[2]

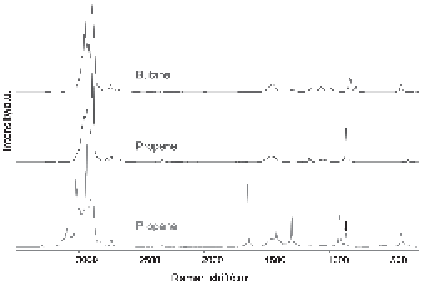

Figure 4: Raman spectra of three common hydrocarbon gases. A weak band near 870 cm^{-1} suggests a minor propane impurity in the propene.

Conclusion

These examples demonstrate that gases can yield high-quality Raman spectra quickly. Furthermore, the Raman spectrum is a unique fingerprint for confirming molecular structure and quantitatively analyzing mixtures. Because IR and Raman spectroscopy are subject to different selection rules, using both techniques is recommended for a comprehensive characterization of a sample. Relying on either technique in isolation could give a misleading impression of the composition. This note also demonstrates that Raman spectroscopy allows observation and quantitation of homonuclear diatomics, which are not accessible to IR analysis. Note also that Raman spectroscopy is a very useful tool to support REACH registration of solids and liquids.

Reference

1. www.hse.gov.uk/reach/about
2. Schrader, B. *Raman/Infrared Atlas of Organic Compounds,* VCH: New York, 1989.
3. Marowsky, G., et al. Applied Physics B, 39, 1986, 47–53

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