Electronics And Instrumentation

8th Semester

Subject: Analytical Instrumentation
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Unit-2

Chromatography/ Fourier Transform Infrared Spectroscopy

The combination of chromatographic separation with Fourier transform infrared spectroscopy has significantly improved the analysis of complex mixtures . In chromatography/ FT-IR systems, an infrared detector providing information on the structure of separated species is used instead of standard bulk chromatography detectors such as thermal conductivity, flame ionization, ultraviolet, or fluorescence; these detectors can be used for quantitative analysis when the identities of the mixture components are known. In these systems the following factors must be taken into consideration: the physical state of the matter to be analyzed, the optimization of the interface between chromatograph and FT-IR, and the specific requirements and constraints of all three parts. In gas chromatography (GC)/FT-IR spectroscopy , one type of interface is composed of temperature-controlled, long, thin flow through gas cells or "light pipes" coated with gold for high reflectivity. As the light-pipe techniques have a detection limit in the nanogram range, subnanogram limits can be routinely attained with the matrix-isolation technique (GC/MI/FT-IR) , and even better detection limits are achieved with the subambient trapping GCR-IR technique. Rapid-scanning interferometers able to record the entire spectrum in less than one second at low resolution (usually 4 or 8 cm-'), together with highly sensitive detectors (e.g., cooled MCT detectors), are essential in all column ChromatographyFT-IR spectroscopic techniques, with capillary GC/FT-IR requiring the most rapid data acquisition. In comparison to vapor phase species, rotations of matrix-isolated species are hindered, which results in sharper and more intense intense bands. Hence, for accurate spectra representation, GC/MVFl-IR spectra are usually measured at 1 cm-' resolution. The Gram - Schmidt vector orthogonalization method is the most sensitive and computationally most efficient and, hence, the most popular procedure for the reconstruction of the total chromatographic trace from interferometric infrared data. Selective detection is obtained by functional-group-specific chromatograms (chemigrams), which are produced by computing absorbance spectra during chromatographic separation and plotting integrated absorbance for prespecified wavelength windows as a function of separation time, representing the quantity of a specific functional group that elutes as a function

time. In ChromatographyR-IR spectral evaluation, in order to classify unknowns as to compound type, library searching has proved to be very useful. The addition of a complementary detector significantly increases the power of GC/FT-IR analysis. Mass spectrometry (MS) is an ideal choice because the disadvantages of each method-infrared spectroscopy often cannot distinguish between long-chain homologues, and mass spectrometry frequently fails to distinguish isomeric species-are offset by the other. The crucial point in liquid chromatography (LC)/FT-IR methods, however, is the interferences caused by the liquid phase. Actually, two viable LC-IR systems are commercially available: the LC-Transform and the InfraRed Chromatograph (IRC) . While the LC-Transform is a solvent-elimination interface, the IRC provides full IT-IR spectra of the eluent stream from an LC column. The LC-Transform system utilizes a high-performance ultrasonic nebulizer or a pneumatic linear capillary nozzle to remove the mobile phase from samples as they elute from the chromatograph. The capillary is surrounded by hot, flowing sheath gas which provides sufficient thermal energy to evaporate the mobile phase and to contain the nebulized spray in a tight, focused cone as the spray emerges from the nozzle. The sample is deposited on a germanium sample-collection disk as spots with diameters between 0.5 and 1 mm. In a consecutive, uncoupled step, good quality infrared spectra can be obtained from these spots, which contain microgram to sub-microgram amounts, by the use of a specially designed optics module, comprising a beam condenser. While this optics module can be used in any FT-IR spectrometer uncoupled from the LC-Transform interface, the IRC includes an FT-IR spectrometer, a data station for driving the spectrometer and for data processing, and a vacuum interface for depositing and scanning the sample. Being a real-time direct deposition interface, the IRC uses an ultrasonic nebulizer, a desolvation tube and a vacuum chamber to evaporate the solvent from the LC stream. The sample residue is then deposited onto a moving zinc selenide window. The data station collects a continuous array of spectra as the dry sample track on the window moves through the focused beam of the spectrometer.

Near-Infrared Spectroscopy

Comparison of Mid-Infrared and Near-Infrared Spectroscopy

Near-infrared spectroscopy as a valuable tool for qualitative and quantitative analysis has experienced a revival through the development of chemometric methods and the introduction of fiber optics during the 1980s, and highquality near-infrared spectra are provided by improved conventional and by Fourier transform instruments.Various aspects differentiate a mid-infrared spectrum

from the corresponding near-infrared spectrum . In the mid-infrared region fundamental molecular vibrations always occur between 4000 and 200 cm-', while in the near-infrared region overtones and combination bands of these fundamentals are observed between 12 800 and 4000 cm-'. Near-infrared bands are due primarily to hydrogenic stretches of C-H, N-H, and 0-H bonds whose fundamental vibrations give rise to strong bands between 4000 and 2000 cm-I, so that their overtones and combinations occur above 4000 cm-' as the most intense absorption bands in the near-infrared spectrum. Since the near-infrared absorptions of polyatomic molecules thus mainly reflect vibrational contributions from very few functional groups, near-infrared spectroscopy is less suitable for detailed qualitative analysis than mid-infrared spectroscopy, which shows all (active) fundamentals and the overtones and combinations of low-energy vibrations. The near infrared overtone and combination bands depend more on their environment than does the fundamental of the same vibration; slight perturbation in the bonding scheme causes only small changes in the fundamental but significant frequency shifts and amplitude changes in the near-infrared. In going from the fundamental to the first overtone the intensity of an absorption band decreases by a factor of about 10- 100, so that the sensitivity of near-infrared spectroscopy is reduced in comparison with the mid-infrared. This is a disadvantage when gases are to be measured, but for liquids, it is a considerable advantage as regards sample handling because cells with convenient path lengths between I mm and lOcm can be used. Glass or quartz is used as window material. Near-infrared bands of liquids and solids have relatively large bandwidths between 30 and 60 cm-I, so that they strongly overlap and direct assignment of bands is generally not possible for larger,

complex molecules. This is why, in the near-infrared, easy quantitative analysis using isolated bands, as in the mid-infrared, is not possible. Chemometrics , however, by the application of mathematical and statistical procedures, generates correlations between experimental data and the chemical composition or physical properties of the sample, and can be used in a general manner to solve quantitative and qualitative analytical problems.

Applications of Near-Infrared Spectroscopy

Applications of near-infrared spectroscopy include chemistry the oil industry, clinical analysis, biological and medical analysis, and the pharmaceutical industry . Since the intensities of characteristic near-infrared bands are independent of or only slightly dependent on the state of the system, near-infrared spectroscopy is widely applicable for the quantitativestudy of liquid and compressed gaseoussystems, including fluid systems, up to high pressures

and temperatures. The application of near-infrared data to routine quantitative analysis was initiated by NORKIS, who used diffuse reflectance measurements to quantitatively determine major components, such as moisture, protein and fat, in agricultural commodities. In comparison with mid-infrared, near-infrared diffuse reflectance is able to measure powdered samples with minimal sample preparation, and lends itself extremely well to quantitative analysis because the smaller absorptivities and larger scattering coefficients at shorter wavelengths result in a larger scattering/absorption ratio. Although near-infrared reflectance analysis was initially developed for agricultural and food applications , in combination with chemometrics it is now applied to many other areas, e.g., polymers , pharmaceuticals , organic substances , geological samples , and thin-layer chromatography .

The excellent transmittance of quartz in the near-infrared range has led to a further enhancement of the potential of near-infrared spectroscopy by the introduction of fiber optics. Fiber-optic waveguides are used to transfer light from the spectrometer to the sample and, after transmission or reflection, back to the spectrometer. Most fiber optic cables consist of three concentric compo nents: the inner part, through which the light propagates, is called the core, the middle layer is the cladding, and the outer protective layer is the jacket. Crucial to the light throughput of the fiber optic cable are the optical properties of the core and cladding. The difference in refractive index of the two materials defines the highest angle at which the core kladding interface exhibits total internal reflection, and hence allows the light to propagate through the cable. This angle is related to the numerical aperture (N.A.) of the fiber by the following equation:

$$\sin\alpha = \text{N.A.} = \left(n_{\text{core}}^2 - n_{\text{cladding}}^2\right)^{1/2}$$

where 'x is the half-angle of acceptance and n is the refractive index of the material. The greater the difference in refractive index the greater the halfangle of acceptance. Any light entering at an angle greater than the half-angle of acceptance is lost to the cladding through absorption. The core and cladding are usually of quartz (of different refractive index), while the outer protective layer is a polymer; other fiber optic materials are zirconium fluoride (ZrF) and chalcogenide (AsGeSe) .The obvious advantage of the optical fiber technique is that the location of measurement can be separated from the spectrometer by between two and several hundred meters, depending on the length of the waveguide. Since almost all practically relevant substances show characteristic nearinfrared absorption bands, quantitative analysis by near-infrared spectroscopy is generally applicable to on-line concentration measurements in connection with chemical reactions, chemical equilibria, and phase equilibria.

Various probes can be integrated into different reactors or bypasses and offer numerous remote-sensing and on-line process control applications. In the analysis of hazardous or toxic materials this has proved of outstanding importance. In the refining, petrochemical, polymer, plastics, and chemicals industries, typical applications of near-infrared remote spectroscopy are the determination of the octane number and oxygenates in gasoline, aromatics in fuels, the composition of solvent mixtures the hydroxyl number of polyols, low contents of water in solvents, and for polymer analysis.