UV Analysis - General Theory

UV ANALYZERS

The UV region consists of wavelengths from 200 to 400 nanometers (nm). The visible region extends from 400 to 800 nm, and the near IR (NIR) region covers 0.8 to 2.50 micrometers (j~m). Nanometer units are commonly used in the UV/VIS region, while micrometers or microns are normally used in the NIR region. The UVVIS-NIR is a relatively small part of the electromagnetic radiation spectrum, and the shorter the wavelength the more penetrating the radiation. The region where a compound absorbs radiation depends on the energy of the molecular transitions. High-energy electronic transitions are observed in the low-wavelength UV/VIS regions. Moderate-energy vibrational and rotational transitions are observed in the high-wavelength IR region.

The Main Components Of UV Analyzers

Photometers and spectrophotometers can be used for on-line monitoring of process streams. These essential components are:

1. Source-provides radiation for the spectral region being measured

2. Monochromator-a device used to select narrow bands of wavelengths

3. Sample cell-contains the sample at an appropriate path length

4. Detector-a device which measures transmitted energy and converts it into electrical energy

5. Readout device-provides a means of recording the measurement results

Radiation Sources
The function of the source is to provide radiation of sufficient energy to make measurements in the region of spectral interest.

The cadmium, mercury, and zinc vapor sources that are used in the UV region are emission line sources. The output of these sources provides radiation as narrow discrete emission lines at a high-energy level. Mercury vapor lamps are often used because of their long service life. Deuterium arc sources provide a broad band of UV radiation at all of the wavelengths in the UV region. The energy of the deuterium source is relatively lower than the energy of the mercury source. The two sources used in the visible and NIR regions are tungsten filaments and quartz-halide lamps.

Two types of UV energy sources are used: broad and discrete line emission sources. The broad emission source provides energy in a broad wavelength band, and narrow-band filters are used to isolate the wavelengths of interest. These sources provide all

wavelengths in the region but usually have a low-emission, or low-energy level, at any given wavelength. Sources of this type include hydrogen, or deuterium, discharge lamps; tungsten lamps; and tungsten-iodine lamps.

Discrete line sources use gas discharge lamps with narrow lines of emission. These sources emit radiation energy at various discrete wavelengths at a high-energy level. The wavelengths that are not desired are filtered, leaving only the wavelength of interest. However, the gas discharge lamps are limited to the spectral emissions of mercury, cadmium, zinc and thallium therefore, all wavelengths is not available.

Selection of measuring and reference wavelengths is generally a compromise between the maximum absorbance wavelength of the component of interest and the wavelengths available from the gas discharge lamps. This usually leads to selection of a wavelength on the side of the absorption peak.

Of the radiation sources used in the UV region, the tungsten-filament-type incandescent lamps are the least expensive. These continuous spectrum sources can be used in UV photometers, but they have enough energy only at wavelengths exceeding 350 nm. Tungsten-iodine cycle lamps can be used down to 300 nm. Mercury vapor lamps are the most useful UV sources due to their high intensity and long life (up to 5 years). Medium-pressure mercury lamps can operate down to 300 nm, and low-pressure ones, down to 254 nm. Zinc discharge lamps are useful due to their 214 nm emission line, as are chromium ones for their 228 nm emission line, but they are not as stable as mercury lamps. Hydrogen and deuterium lamps are delicate, expensive, and their lives seldom exceed 3 months.

The Monochromator

Dispersive and nondispersive monochromator are used in photometric analysis. Spectrophotometers are dispersive instruments and photometers are nondispersive instruments. The function of the monochromator is to disperse light from a source and selectively pass a narrow spectral band to the sample and detector. The dispersing element is usually a diffractive grating that is a highly polished mirror with a number of parallel lines scribed on its surface. For each position of the grating a narrow band of dispersed radiation passes through the exit slit. Spectrophotometers are dispersive devices that are used to scan across a spectrum of wavelengths; they can be used to make measurements at several wavelengths. This capability allows for the analysis of multiple components with a spectrophotometer.

Photometers are nondispersive devices which exclude a large amount of spectral radiation. Photometers are used to make measurements at selected discrete wavelengths. Narrow bandpass interference filters are used to pass radiation at selected reference and measurement wavelengths. A typical bandwidth for UV/VIS filters is 10 nm. The typical bandwidth for NIR filters is 20 to 80 nm. The reference wavelength filter is normally selected where none of the components present in the process stream absorb radiation. The measurement wavelength filter is selected to match the absorption band of the component being analyzed. The ratio of the transmitted light at the reference and

measured wavelengths is measured by the photometer. Normally, photometers are used to measure a single component in a process stream.

The Sample Cell

The purpose of the sample cell is to contain a representative sample from the process stream. The major components of the cell are the cell body, windows, and 0-rings. Proper selection of cell materials is very important for the successful application of a process photometer. Stainless steel is the material most commonly used for cell bodies. Other metals such as Monel, Hastelloy, and titanium are also used. Plastic cell bodies made of Teflon or Kynar are used in some applications. Quartz, sapphire, and glass cell windows are used in the UV-VIS-NIR spectral regions. The sealing of the sample in the cell is accomplished with 0-ring gaskets. Viton, ethylene-propylene, and kalrez 0-rings are commonly used in sample cells. An important parameter for the cell is the selection of an appropriate path length. The distance between the windows determines the path length of the cell. Path lengths from 1 mm to 1 m (0.039 in. to 39.4 in.) are used in process photometers. The sensitivity of a photometric measurement is dependent on the path length. For a particular measurement a long path length will provide more sensitivity than a short one.

Detectors

Several types of detectors are used in process UV analyzers, including phototubes, photomultiplier tubes, and photocells.

The photoelectric effect is used in the vacuum phototube to produce a current proportional to the energy striking the tube cathode. A phototube with UV response has a long life and a low-temperature coefficient.

The photomultiplier tube offers very sensitive detection of UV and visible light but large radiation energy levels will damage the light-sensitive surface. This detector has a high-temperature coefficient.

The photocell (photovoltaic) is a semiconductor light detector of the barrier layer type. A current is developed proportional to the light intensity but, unfortunately, the current output is not linear with the energy level. This may not be detrimental when used in a null-balance detection system, and the relative low cost of this device (because a voltage supply is not required) is attractive.

Photomultiplier tubes (PMT) have traditionally been used in UV/VIS instruments. The photoelectric effect is used in the PMT to produce a current proportional to the radiation striking the cathode of the tube. The sensitivity of the PMT can be controlled by adjusting the gain voltage of the photocathode. Silicon photodiodes are semiconductor detectors that are used in the UV/VIS region. Germanium photodiodes are used in the NIR region. Photodiodes are solid-state detectors that are smaller in size and lower in cost than PMT detectors. A recent development in photometric analyzers is the use of photodiode arrays (PDA). The PDA detectors are used throughout UV-VIS-NIR regions. A large number of discrete detectors are located in a very close space in the PDA. This array of diode

detectors allows for all of the wavelengths to be measured simultaneously. The PDA detectors can be used for multicomponent applications. Lead sulfide, germanium photodiodes, and pyroelectric detectors are used in the NIR photometers.

Readouts
Analog meters, digital meters, strip chart recorders, and video display tubes (VDTs) are examples of readout devices used in photometers and spectrophotometers. On-line photometers usually have a 4 to 20 mA option in order to communicate measurement results to a process control computer. Spectrophotometers incorporate a strip chart recorder to record a spectrum of a sample. The spectrum is a plot of percentage transmission or absorbance versus wavelength.

UV Analyzer Designs

There are several proven industrial designs for process UV analyzers:

1. Single-beam

2. Split-beam

3. Dual-beam-single-detector

4. Dual-beam~dual-detector

5. Photodiode

Single-Beam Analyzer
This is perhaps the simplest of the designs and is limited to easy applications. The optical system consists of a source and two phototube detectors. The light source and detectors are so aligned that both detectors receive radiation from the same portion of the source. A sample cell and an interference filter are positioned between one detector and the source. The filter is selected to isolate the wave-bands in which only the component of interest will absorb. The cell length is sized to give an absorbing path adequate for satisfactory sensitivity (i.e., high absorbers require shorter paths). A filter usually identical to the measuring filter is positioned between the source and reference detector.

The amplifier, or control circuit, compares the outputs of the two phototubes, and the difference in their outputs is related to the UV energy absorbed by the sample. The reference detector is used to provide compensation for changes in line voltage and source decay. Process analyzers have been built without this feature, measuring only the energy change at the measuring detector, but these analyzers are subject to drift and are generally unreliable.

The opposed-beam design is a simple, low-cost, moderate-accuracy instrument for simple, low-sensitivity measurements. The output of this instrument is affected by dirt and bubbles in the sample and by drift in the detector circuit.

Split-Beam Analyzer
A single sample cell is located between the source and the detectors. A beam splitter (semitransparent mirror) is used after the sample to create two paths of energy; one beam for the measuring wavelength and one beam for the reference wavelength.

Interference filters and/or broad-band filters are used to isolate the desired wavelengths. The reference wavelength is selected in a region where the component of interest absorbs weakly or, preferably, not at all.

One beam is directed to the measuring photomultiplier (PMT) tube through an optical filter which passes light at the measuring wavelength. The other beam is directed to the reference PMT through an optical filter which passes light at the reference wavelength. The phototubes convert both light signals to electric currents proportional to the light intensity in each beam. The outputs of the phototubes are compared by the amplifier, which provides an output signal that is proportional to the concentration of the measured component. This output signal is reported on the output meter of the control section of the analyzer.

The use of the split-beam design with a reference detector offers the advantage of minimizing, or eliminating, the effect of other weak UV absorbers in the sample. Further, source changes, sample turbidity (dirt or bubbles in the sample), and cell window dirt are seen equally in both wavelengths and do not affect the measurement until the absolute energy intensity drops below the sensitivity of the detector. The three housings of the analyzer are easily separated. The split-beam system offers high sensitivity and accuracy with low drift for most applications, at a moderate cost.

Dual-Beam-Single-Detector Analyzer
The dual-beam-single-detector UV analyzer uses two optical paths, a single sample cell and a single photomultiplier detector. One path includes the sample cell while the other path is used for reference as it does not pass through the sample. The paths are recombined and both pass through an interference filter that isolates the wavelengths selected for the measurement.

An interrupter or "chopper" is used to block the measuring and reference beams alternately. This creates pulses of energy through the sample cell which are 180 degrees out of phase with the energy pulse of the reference beam. These pulses are received by the photomultiplier consecutively and are equal in magnitude with a nonabsorber in the sample cell. When the sample contains the component of interest, the energy pulse intensity and the output of the detector for the measuring pulse are both reduced. The control amplifier receives these pulse outputs and demodulates, or converts, their ratio to a usable analog signal.

This design gives good compensation for source changes and detector drift, but turbid samples and samples leaving a dirt deposit will cause drift. Samples of this nature sometimes require the use of two sample cells and two separate filters one in each path. The filters create a measuring and a reference wavelength as in the split-beam-dual-detector system. The sample cells may or may not experience window coating at the same rate, which only partially solves the drift problem. Use of a "chopper" introduces a moving mechanical member that increases maintenance.

The dual-beam-single-detector system offers high sensitivity and accuracy for moderate cost, but zero drift may occur with "dirty" samples.

Dual Beam Dual Detector Analyzer

The dual-beam-dual-detector design UV analyzer isolates the wavelength used for the measurement before the beam splitter and uses separate phototubes for the measuring and reference wavelengths. This design is a combination of the optics of the dual-beam-single-detector and the detector of the split-beam analyzer From this design, performance similar to that of the dual-beam-single-detector design can be expected; that is, high sensitivity and accuracy for a moderate cost, but "dirty" samples may create drift errors.

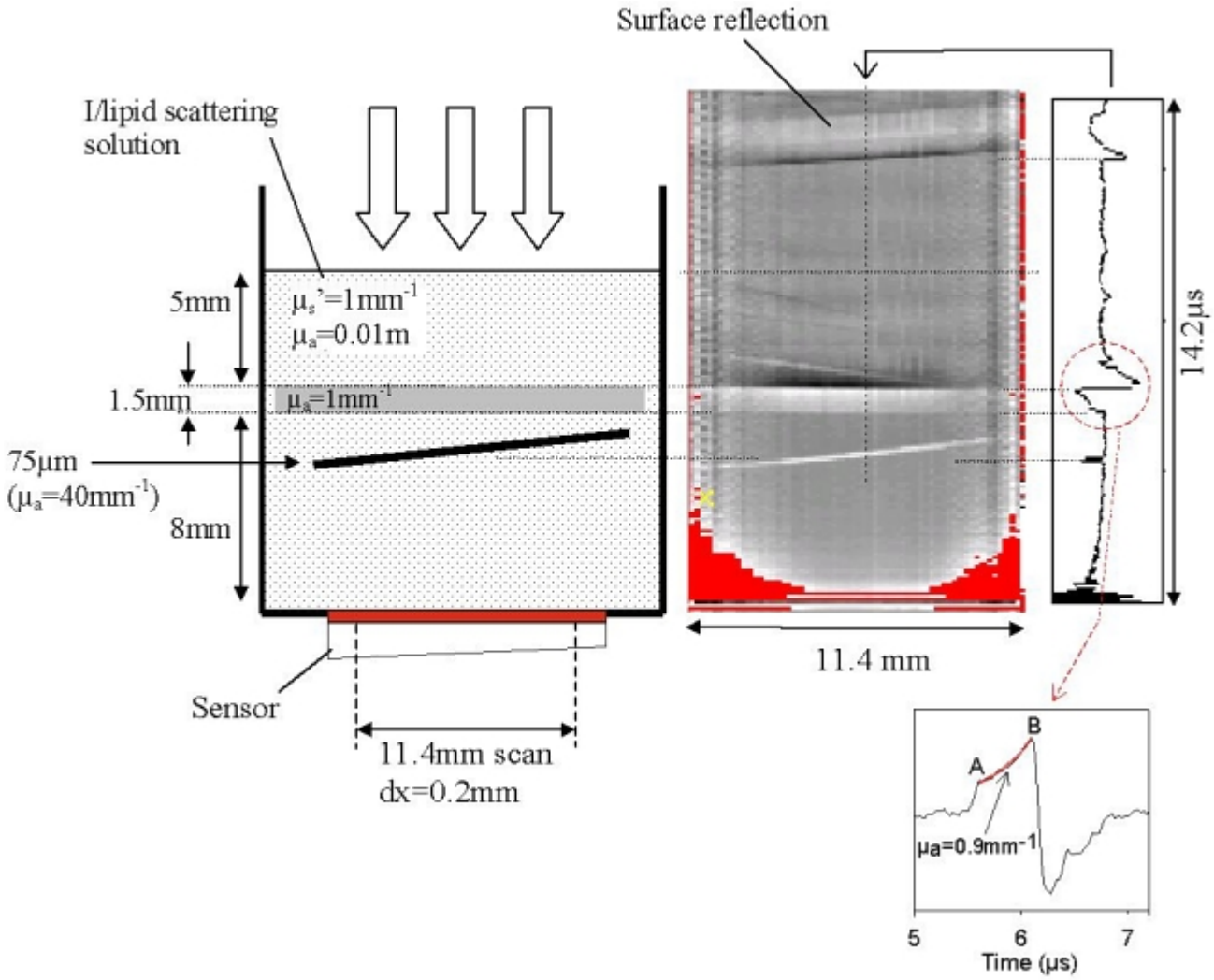
Photodiode Array Photometers

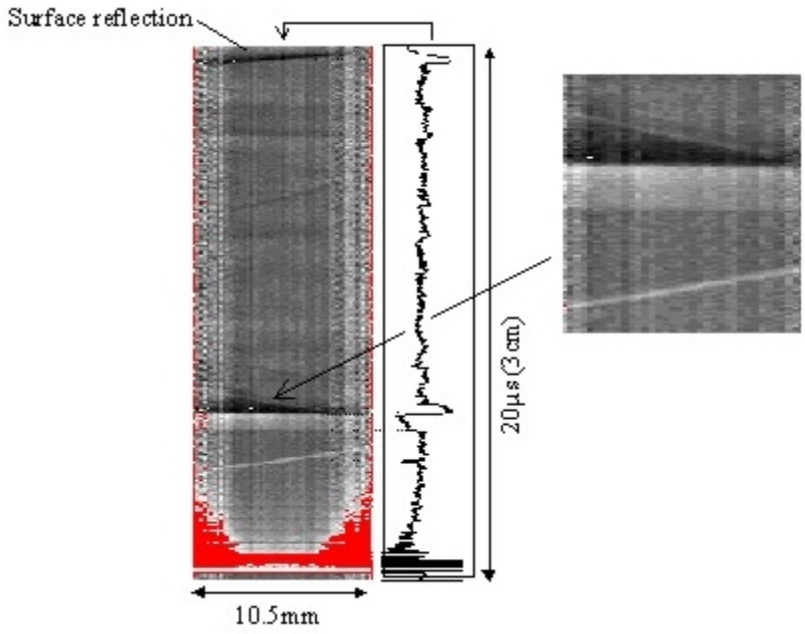
Photodiode array (PDA) spectrophotometers monitor all of the wavelengths in the spectrum simultaneously. The light from the source passes through a lens and a shutter and through the sample cell. The light passes into the detector assembly where it is focused onto a slit and onto a holographic grating which disperses the light which strikes the PDA detector. The diode array detector is a series of linearly spaced Silicon photodiode detectors, which measure absorbance at a specific spectral bandwidth. The advantage of this design is that the spectrum is scanned without any moving parts except for the shutter. Data from the PDA detectors is acquired in parallel, which results in a fast analysis time. Most of the work with PDA detectors has been in the UVIVIS region. The short wavelength NIR region (800 to 1100 nm) is also being investigated with PDA devices. Analyzers are also available that couple fiber-optic cables with PDA devices. Analysis of hydrogen sulfide and sulfur dioxide in sulfur recovery and the determination of octane number are two examples of PDA applications.

Scanning Spectrophotometers

Scanning spectrophotometers are dispersive devices that normally utilize diffraction gratings to scan across a spectral region. Scanning devices can be used for multiple component applications. Scanning spectrophotometers can be used in the UV, visible, and NIR regions.. An important development has been the interfacing of fiber-optic wavelengths with conventional scanning spectrophotometers. The optical waveguide is usually a single fiber-optic cable. An advantage of using fiber optics is the elimination of the sample handling system. In the fiber-optic design the polychromatic light from the source passes through lenses and filters and onto the fiber-optic cable. The light is transferred along the cable to the sample probe. The sample-modified light is then collected by a second fiber cable and transferred to the monochromator where it is diffracted into individual wavelengths and measured by the detectors. The data from the

analyzer are processes on a personal computer (PC). Use of the PC allows for the use of multivariate calibration techniques such as partial least squares (PLS). The measurement of multicomponent solvent mixtures and the determination of octane number for gasoline samples are two typical applications performed on fiber-optic scanning spectrometers.





luminescence, near-infrared semiconductor laser fluorescence, and HPLC-mass spectrometry

http://www.spectroscopynow.com/Spy/basehtml/SpyH/1,1181,3-5-1-0-1-book_new_detail-0-661,00.html

Luminescence

A general term which describes any process in which energy is emitted from a material at a different wavelength from that at which it is absorbed. It is an umbrella term covering fluorescence, phosphorescence, and triboluminescence.
Luminescence phenomena often occur only in the presence of a trace amount of an activator species (such as iron in the case of manganese-containing salt from the Saltan Sea), which causes the manganese and lead to interact quantum mechanically to give an excited manganese state which would otherwise be inaccessible. Quenchers such as iron and copper may also destroy luminescence. A final source of luminescence can be lattice defects in materials such as diamonds.
Chemiluminescence, Fluorescence, Triboluminescence

Fluorescence

A luminescence phenomenon in which electron de-excitation occurs almost spontaneously, and in which emission from a luminescent substance ceases when the exciting source is removed. In fluorescent materials, the excited state has the same spin as the ground state. If denotes an excited state of a substance A, then fluorescence consists of the emission of a photon, where h is Planck's constant and is the frequency of the photon. The quantum yield of a fluorescent substance is defined by Fluorescent Lamp, Luminescence, Opalescence, Phosphorescence

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