

Incoming Materials Validation by UV/VIS/SWNIR Absorbance; An On-line Recognition Method

Introduction

Identifying the composition of incoming materials is significant both in terms of economy and safety. Ideally, the stream is analyzed in great detail, instantaneously and on-line. However, it is rarely possible in practice; often the various types of raw materials need to be analyzed which might require a range of analytical techniques. Analysis time is an issue, as is cost of purchase and maintenance of the different analyzers. Instead of performing a complete analysis of the stream, a method in which the stream composition is "recognized" is described.

Recognition Method

The following application required a method to differentiate between xylenes and all other possible aromatic streams. A NIR spectrum of all samples was measured and a recognition factor defined.

A computational routine is used to compare between two spectra while eliminating amplitude variations. The amplitudes at two points are rematched, the normalization point and the internal reference point. The second spectrum is then subtracted from the first, resulting in a residual spectrum. The recognition value is calculated over the wavelength range specified in the method definitions. The normalization factor (N) is the ratio of the absorbancies (y-values) of the two spectra at the normalization wavelength (Y_{np}) corrected by the absorbancies (y-values) at the internal reference wavelength (Y_{irp})

$$N = \frac{Y_{npB} - Y_{ipB}}{Y_{npA} - Y_{ipA}}$$

The normalization factor is then used to calculate the y-values for the residual plot:

$$Y_{\text{residual}} = \frac{Y_B - (N Y_A)}{Y_{npB} - Y_{ipB}}$$

By dividing the absorbance values by the absorbance value of spectrum B at the normalization wavelength, the intensity of both spectra are set to unity at the normalization wavelength. The difference is then independent of the amplitudes of the original spectra.

The recognition factor is calculated from the residual spectrum, as the sum of squares of the residual value divided by the sum of the variances of each of the y-values in the original spectra over the specified wavelength

$$R = \frac{\sum Y^2_{\text{residual}}}{\sum (V_A + V_B)}$$

range:

Two identical spectra give a recognition value of 0; the higher the value, the less similar the spectra.

SWNIR Absorbance Spectra

An essential method requirement was that it spanned a large absorbance dynamic range. Figure 1 shows the absorbance spectrum (200-1100nm) of mixed xylene. It can be seen that the absorbance in the low UV is very high, whereas the SWNIR region is within the measurements range. The SWNIR spectral region was therefore chosen. The SWNIR spectrum of various samples that might be present in the stream were measured and are shown in figure 2.

A diode array process analyzer was used to measure the absorbance spectra of various aromatic samples; Figure 3 shows the comparison or residual graphs of several samples compared with the mixed xylene. Table I gives the recognition factor for all samples.

On-line monitoring

An industrial UV/VIS/SWNIR diode array spectrophotometer was used to measure the absorbance spectra of the samples.^(1,2,3) The Spectrophotometer was then installed on-line to continuously measure the absorbance spectrum of the stream. The diode array spectrophotometer was not used as a composition analyzer,^(4,5,6) as frequently done, but rather a pattern recognition monitor. Hence, the process of data collection for calibration purposes was not required.⁽⁷⁾ The absorbance spectrum of the mix xylene was stored (spectrum A) and then continuously compared via the normalized compare procedure to the absorbance spectrum of the stream (spectra B). The recognition factor was then sent to the 4-20mA output. A preset threshold value was set so that when exceeded, an alarm would be activated, informing the plant that the wrong material is on-line.

Composition Monitoring

Often following the validation of the incoming stream, the concentration of the stream components are required. The spectra are then analyzed to give the composition of the stream and to output these values continuously via a pre defined communication protocol.

Conclusion

It can readily be seen, in the absorbance spectra shown in Figure 2, that there are significant differences in spectral features between the mix xylene and the Fawley xylene and the other samples. To automate the process of distinguishing between mix xylenes and other samples an algorithm was implemented to compute, from the measured spectra, a recognition factor. Figure 3 shows the residual spectrum enhancing the differences while eliminating variation due to amplitude differences.

This application required a high-resolution⁽⁸⁾ full spectral analysis allowing for the detection of small structural variations in the spectrum. The analyzer needed to

be immune to wavelength drifts, which might have resulted in a recognition factor drift. Hence, a diode array based spectrophotometer is imperative, providing a full spectral analysis instantaneously, and eliminating any wavelength drift associated issues because it is a solid-state device with no moving parts. An added benefit can be appreciated; when alternating the referenced in-coming material, only a user defined parameter needs to be modified, allowing for a very versatile technique.

A diode array process UV/VIS/SWNIR spectrophotometer was utilized to continuously measure the absorbance spectrum of the in-coming material, verifying the contents of the stream. This validation technique can be applied to a variety of applications, provided that the substance to be referenced against has a unique UV/VIS/SWNIR absorbance spectrum.

Figure 1: Absorbance spectrum of mixed xylene (1 cm path blank - water)

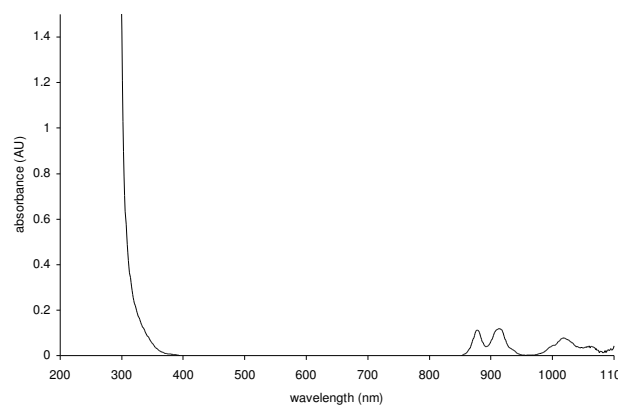
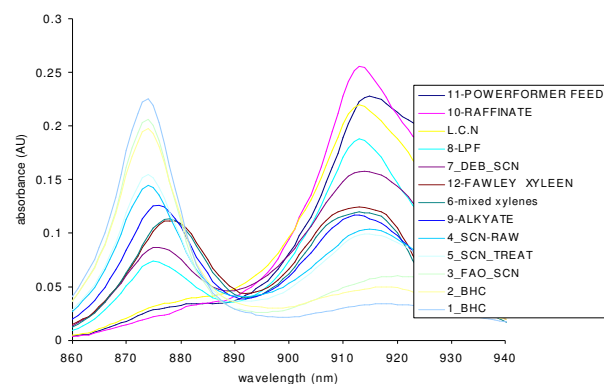


Figure 2: absorbance spectrum of aromatic mixtures that might be present in the stream (1 cm path, blank-water)



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Figure 3: Residual spectra A= mixed xylene, B aromatics

