Sampling Considerations for the Measurement of a UV Stabilizer in Polymer Pellets Using FT-NIR Spectroscopy

Emiliano Genorini, Thermo Optek Italia, Milan, Italy
Mark Kemper and Leza Luchetta, Thermo Nicolet, Madison, WI

ISN-0028

Keywords
Additives
Antaris
FT-NIR
Polymer
Polystyrene
Sample Cup Spinner

Abstract

For heterogeneous samples such as polymer pellets, it is critical to obtain a measurement that is representative of the bulk sample and not just a small fraction of the material. This is often a significant challenge when using traditional near-infrared spectroscopy sampling methods. Accessories such as the Sample Cup Spinner allow a greater amount of material to be analyzed in an automated device. In this study, two diffuse reflectance-sampling methods were compared to determine the most efficient and accurate method for sampling polystyrene pellets. A single calibration model was developed to determine the concentration of an ultraviolet (UV) stabilizer additive in polystyrene pellets. Using the two sampling methods, the concentrations of four unknown samples were determined using the single model. The results demonstrate that the Sample Cup Spinner accessory provides the optimum performance with the shortest analysis time.

Introduction

With the high production rates in the polymer industry, it is essential that a quick, accurate, and easy-to-use analytical technique is available to monitor the quality of the material produced. Traditional methods, such as titration or extraction followed by GC, require sample preparation by a trained technician and often deliver results to the production personnel after a significant time lapse. This time lag between sampling and the completion of the analysis can produce out-of-specification material, resulting in manufacturing inefficiency, high scrap levels and the need to rework product that does not meet quality standards.

Fourier transform near-infrared (FT-NIR) is an ideal tool for at-line or near-line quality control analysis of polymer pellets. It offers several advantages over traditional quality control techniques including:

- Availability of answers in minutes allowing quicker feedback to the production personnel and improvement of process efficiency
- Ability to perform analyses at-line
- No sample preparation
- Elimination of the need for purchase and disposal of hazardous reagents
- Improved operator-to-operator reproducibility
- Reduced cost of quality control testing
- Non-destructive testing making the samples available for analysis by other techniques

For heterogeneous materials such as polymer pellets, a small sample may not be representative of the bulk material. Each pellet or group of pellets may have a slightly different composition than the next. For this reason, a representative sampling method is needed. This is often achieved by the use of a cup with a quartz window. The sample cup provides a way to analyze greater amounts of material without having to empty the first sample and replace it with a new sample from the same batch. Once the sample is placed in the cup, it can be analyzed by two methods.

1. Using the Sample Cup Spinner (Figure 1), the sample can be continuously rotated constantly exposing new sample to the incident beam during data collection. A single spectrum is obtained that is representative of the material in the cup. The Sample Cup Spinner allows the largest volume of material to be analyzed in a single measurement.

Figure 1: Sample Cup Spinner for Antaris® FT-NIR analyzer

If a much larger volume of material needs to be analyzed to obtain representative results, the Bulk Polymer Autosampler is an alternative sampling method to consider. As shown in Figure 2, the autosampler carousel, specifically designed for polymer pellets and coarse samples, is filled with the sample. The sample is automatically analyzed point by point to obtain an average result.

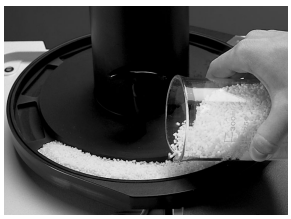

Figure 2: Bulk Polymer Autosampler

2. Multiple single point measurements can be collected at different sample locations within the cup. Multiple spectra are produced for each sample and the results averaged to obtain a representative answer. In order to obtain a representative answer, the user must manually rotate the cup then collect a spectrum. This process must be repeated several times to ensure that the results will be indicative of the entire batch.

The purpose of this study was to evaluate these two diffuse reflectance-sampling methods and determine the most efficient and accurate method for measuring the amount of a UV-stabilizer additive in polystyrene pellets.

Experimental

A set of 17 polystyrene pellet samples were obtained from a proprietary source. The concentration of a UV-stabilizing additive ranged from 42% to 58% by weight. The pellet shapes and sizes varied slightly from sample to sample. The samples were placed into the open powder sampling cup, which has a 47.8 mm quartz window, and analyzed by diffuse reflectance using the integrating sphere module of the Antaris FT-NIR analyzer (Figure 3).

Figure 3: Antaris FT-NIR Solid Sampling System with Sampling Cup Spinner

The Antaris integrating sphere provides a highly efficient method for collecting diffuse reflectance data for solid samples such as polymer pellets. A background was collected for each sample using the internal gold reference of the integrating sphere. The internal reference allows the background to be collected even if the sample cup is in place. Using Thermo Nicolet's RESULT™ data collection software, all spectra were acquired at 8 cm^{-1} resolution and 16 scans with a collection time of less than 15 seconds. Spectra used to develop the method were obtained using the Sample Cup Spinner accessory. The Sample Cup Spinner was adjusted so that the largest amount of sample possible passed through the NIR beam in one complete revolution. Thirteen of the samples were used to develop the FT-NIR model and four samples were used to validate the performance of the model using the two sampling methods.

Once the model was developed, the validation samples were analyzed and the concentration of the additive determined 30 times each using the Sample Cup Spinner and the manual single point measurement technique. To accomplish$the manual single point analysis, the sample was manually rotated approximately 40 degrees between each successive measurement.

Thermo Nicolet's TQ Analyst™ quantitative analysis software was used for all chemometric modeling. A cross-validation using a leave-one-out protocol was used to confirm the results obtained for the calibration.

Results and discussion

One spectrum was collected for each of the samples in the calibration set, 13 samples total, using the Sample Cup Spinner accessory (Figure 4).

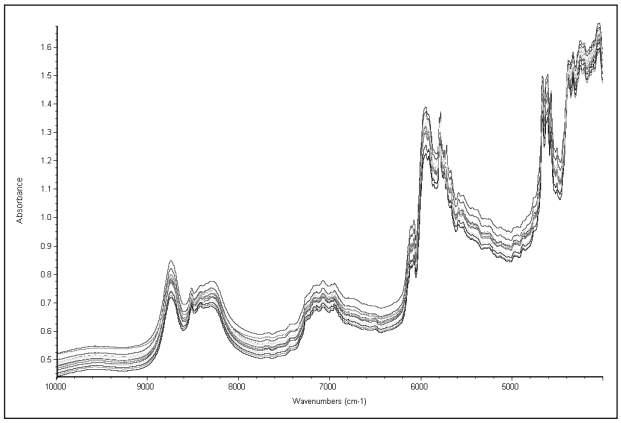

Figure 4: Calibration spectra obtained using the Sample Cup Spinner

The total analysis time for each sample was about 15 seconds. The second derivative spectra of the calibration samples were used to develop the chemometric model (Figure 5).

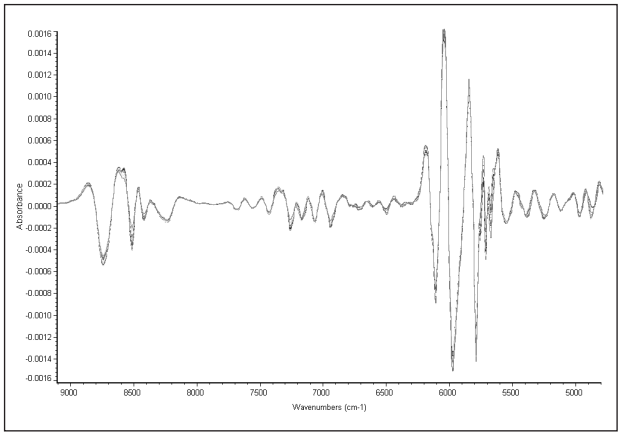

Figure 5: Second derivative spectra

A Norris second derivative (5 segment, 0 gap) was used to pre-treat the data. A two-term Stepwise Multiple Linear Regression (SMLR) model was constructed. Using data points of 7332 and 5091 cm^{-1}, a correlation coefficient of 0.9995 and RMSEC of 0.147 weight % were obtained (Figure 6). The first data point (7332 cm^{-1}) of the SMLR calibration is in the first overtone region and the second point at 5091 cm^{-1} is in the combination band region. A cross-validation using the leave-one-out protocol gave an RMSECV of 0.179 weight %.

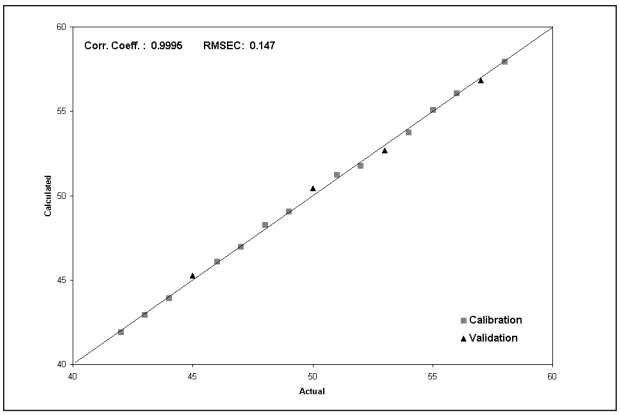

Figure 6: Calibration results using the Sample Cup Spinner

The additive concentration in the validation samples was determined using the SMLR model. The RMSEP (Root Mean Square Error of Prediction) was 0.302 weight % for the samples analyzed using the sample cup spinner. The results obtained using the Sample Cup Spinner and the manual single point measurement techniques were compared. The spectra obtained using the Sample Cup Spinner and the single point measurements are shown in Figures 7 and 8, respectively. Upon visual inspection, the spectra collected using the Sample Cup Spinner are more reproducible than those collected using the single point sampling method. The variability seen with the single point measurement method is expected because each spectrum represents only a fraction of the sample and does not account for the heterogeneity of the material. The Sample Cup Spinner continuously rotates multiple areas of the cup through the NIR beam, therefore the single spectrum that is obtained better represents the bulk of the material.

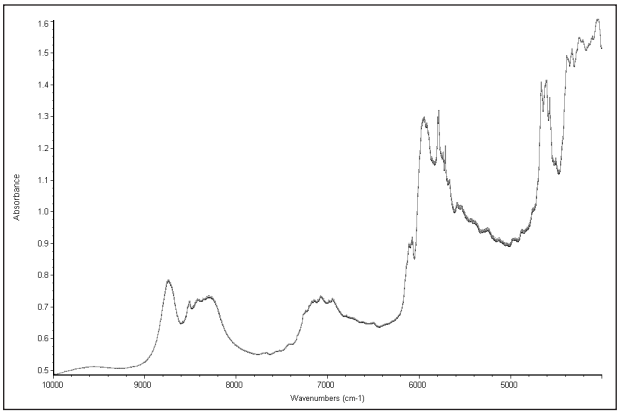

Figure 7: Spectra of unknown sample obtained using Sample Cup Spinner

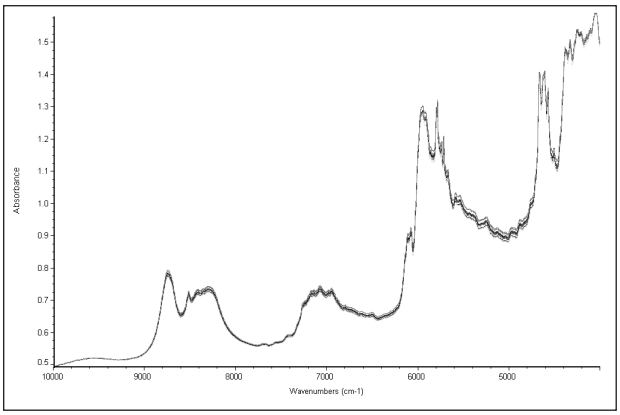

Figure 8: Spectra of unknown sample obtained using single point measurement method

Comparison of the standard deviation of the predicted values obtained using the Sample Cup Spinner and the single point manual measurements clearly demonstrates that the Sample Cup Spinner is more reproducible and more accurately predicts the additive concentration in the validation sample (Table 1). The standard deviation of the results obtained using the single point measurement technique is two times more than that obtained using the Sample Cup Spinner. The variability in the results between the two sampling techniques for the 30 measurements is presented graphically in Figure 9.

	EXPECTED VALUE	SAMPLE CUP SPINNER	SINGLE POINT MEASUREMENT
Validation Sample 1	57	56.84	55.78
Validation Sample 2	53	52.69	51.97
Validation Sample 3	45	45.26	44.52
Validation Sample 4	50	49.33	49.08
Standard Deviation – Validation Sample 4		0.29	0.62
% Relative Standard Deviation – Validation Sample 4		0.59	1.27
Range – Validation Sample 4		1.18	2.44

Table 1: Prediction results for additive concentration (weight %)

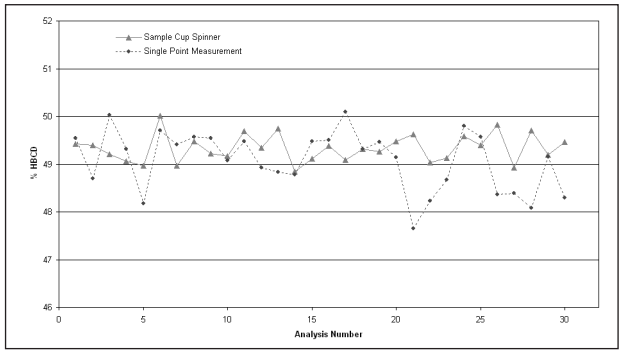

Figure 9: Variability of Sample Cup Spinner results versus single point measurement for sample 1

Conclusions

The Antaris FT-NIR analyzer offers an excellent alternative to traditional methods for determination of additive levels in polystyrene. The main advantage of FT-NIR spectroscopy is that production efficiency is enhanced due to the quicker availability of reliable data. By using the Sample Cup Spinner the analysis time is reduced. By allowing a greater volume of sample to be analyzed, the Sample Cup Spinner provides more representative information on a heterogeneous sample and eliminates the need to analyze multiple samples from the same lot to obtain a representative result.

A Thermo Electron business
5225 Verona Road • Madison, WI 53711-4495 • U.S.A.
TEL: 800-201-8132, 608-276-6100 • FAX: 608-273-5046
E-MAIL: nicinfo@thermonicolet.com
WEB: www.thermo.com/nicolet

ISN-0028 10/02

Thermo Nicolet