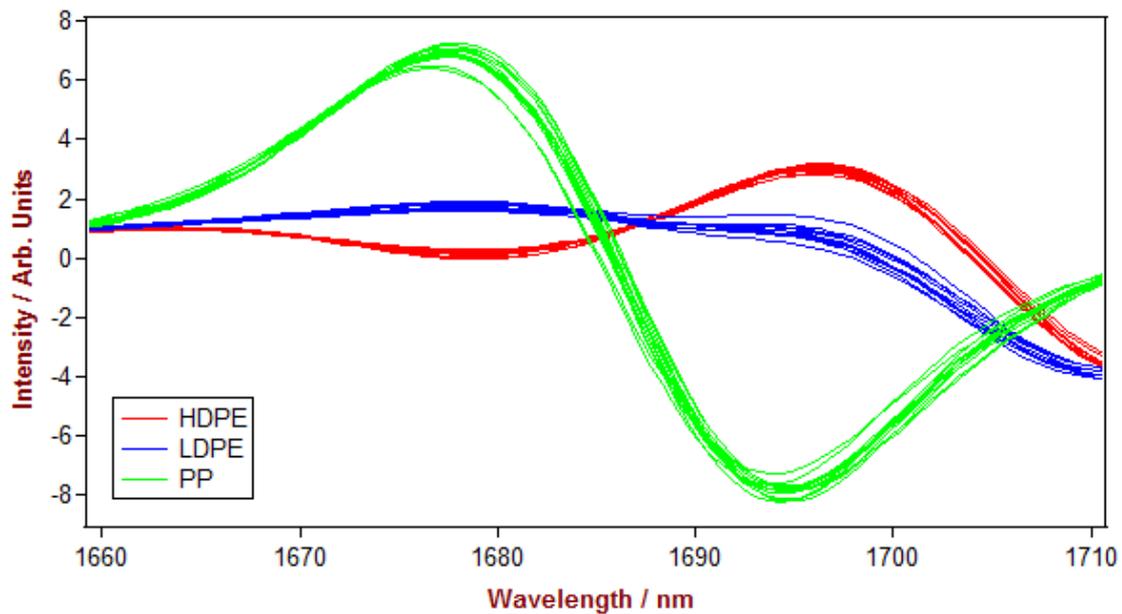


# Analysis of polymer granulate by near-infrared spectroscopy



This Application Note shows that fast near-infrared spectroscopy (NIRS) accelerates quality control of polymer granulates and raw material identification. Polyethylene (PE) and polypropylene (PP) can be simultaneously identified. Additionally, the density of PE is determined in the same measurement.

# Method description

## Introduction

The most commonly used polymers for daily life products are polypropylene (PP) and polyethylene (PE). These polyolefins are versatile and cheap in production costs. PP and PE are used in the same application fields, but due to a lower glass transition temperature, PE is unusable above 80 °C. The broad application possibilities of PE is based on the varying number of cross-links (branches) and therefore also on the density. Depending on its density, PE can be subdivided into:

- Low density (LDPE): 0.915 – 0.935 g/ cm<sup>3</sup>
- High density (HDPE): 0.936 – 0.970 g/ cm<sup>3</sup>

Normally, this parameter is determined according to ASTM D1505/ ISO 1183.

Besides the quantitative characterization of PE, the raw material identification of PP, HDPE and LDPE needs to be assured, especially if the final product will be used as packaging material for food and drug products (regulated according to e.g. FDA and USP).

This application note demonstrates that the fast and cost-saving near-infrared spectroscopy (NIRS) can be used during quality inspection of polymer granulates at the producer and for raw material identification at the end-user to receive simultaneous results for identification and quantification with a single measurement.

## Experimental

### Identification of LDPE, HDPE and PP

For this application 14 samples of HDPE, 11 samples of LDPE and 14 samples of PP granulate were measured on an NIRS DS2500 Analyzer (Tab. 1 / Fig. 1). The spectra were collected in reflection mode over the full wavelength range (400 nm – 2500 nm). The samples were placed into large sample cups, which makes filling and emptying much easier compared to smaller glass vials or cups. The spectra were acquired in moving mode to scan the sample at 8 different positions to generate an average spectrum. The averaging of scans at eight different position covers spectral variation caused by differing granulate shapes and surfaces.

### Quantification of density values in PE

The same 11 samples of LDPE and 14 samples of HDPE granulate were used to develop a calibration model for the quantification of density. The reference values necessary for the development of a quantitative model were provided by the customer using their lab reference analytics.

Tab.1: Used equipment

Equipment	Metrohm code
NIRS DS2500 Analyzer	2.922.0010
NIRS DS2500 large sample cup	6.7402.050
Vision 4.1	6.6069.412



Fig. 1: A NIRS DS2500 Analyzer was used to collect the spectral data in reflection mode over the full wavelength range of 400 – 2500 nm. The large sample cup was used to average the spectral information taken at eight different spots of the polymer granulate.

## Results

### Identification of LDPE, HDPE and PP

In Vision (Metrohm chemometrical software), using the algorithm of correlation in wavelength space with a threshold of 0.95, a library for LDPE, HDPE and PP was developed. Shortened wavelength range (1335 – 1355 nm, 1650 – 1740 nm and 2250 – 2280 nm) were chosen. The spectral data were pretreated using a 2<sup>nd</sup> derivative combined with a Standard Normal Variate (SNV) to get rid of light scattering effects caused by the granulates. Internal cross-validation (leave-one-out method) was applied to verify the performance of the derived library.

## Method description

Fig. 2 show the wavelength region 1660 – 1710 nm, where LDPE, HDPE, PP show clear spectral variations that can be used to differentiate them.

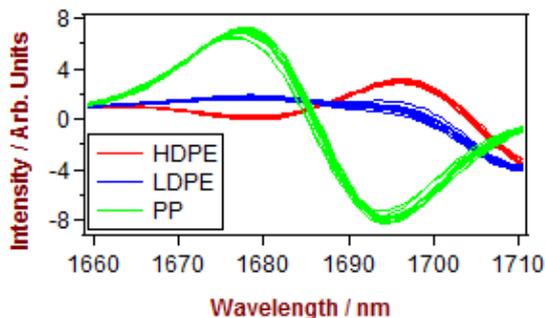


Fig. 2: Wavelength range from 1660 nm – 1710 nm of the 2<sup>nd</sup> derivative + SNV spectrum of PP (dark blue), HDPE (light green) and LDPE (red). The different polymer types (PE and PP) and differences in density values (LDPE and HDPE) influence the spectral shape and the absorbance intensity in a way that an identification without ambiguity is possible.

The Figures Of Merit (FOM) shows a good correlation ( $R^2 = 0.9648$ ) between predicted and calculated values. The comparison of the standard errors of calibration and validation (SEC = 0.0029 g/cm<sup>3</sup>, SECV = 0.0032 g/cm<sup>3</sup>) indicates that the model can be used to predict the density value of PE granulates. A few more samples in the range 0.925 – 0.945 g/cm<sup>3</sup> might increase the robustness and accuracy of the model.

### Conclusion

Near-infrared spectroscopy is a great tool to get simultaneously results for identification and quantification in quality control of PE and PP granulates fast and easily. The project could be expanded with further parameters like melt flow index, crystallinity, melting point or molecular weight.

### Quantification of density values in PE

A Partial Least Squares (PLS) algorithm, was used to develop quantitative prediction model for density values in the range of 0.919 – 0.963 g/cm<sup>3</sup>. Therefore, the whole absorption spectrum from 400 nm – 2500 nm was used. The spectral data were pre-treated using a 2<sup>nd</sup> derivative combined with SNV. Internal cross validation was applied to verify the performance of the derived quantitative model. The result of predicted values versus reference values can be seen in Fig.3.

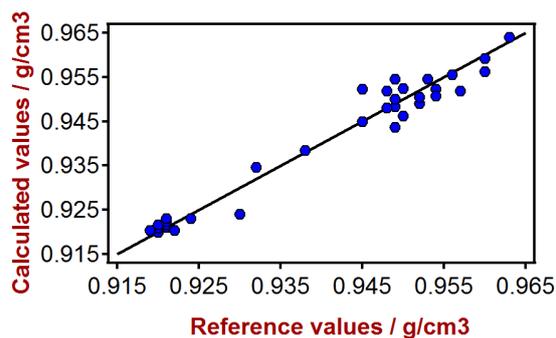


Fig. 3: Correlation of the NIR predicted values with the reference data as a result of a quantitative method development of the density value of PE granulates.