

Application Note AN-NIR-023

Determination of diethylene glycol, isophthalic acid, carboxyl end group, and more in PET with NIRS

Simultaneously monitor multiple quality parameters in virgin and recycled polyethylene terephthalate without chemicals

Determining diethylene glycol content, isophthalic acid content, intrinsic viscosity (ASTM D4603), and carboxyl end group (CEG) in polyethylene terephthalate (PET) is a lengthy and challenging process due to the sample's limited solubility and the need to use different analytical methods. NIR spectroscopy (NIRS) can analyze PET in a few seconds without sample preparation or using any chemical reagents. This study shows that the OMNIS NIR Analyzer provides a fast, cost-efficient solution to simultaneously determine all these QC parameters in PET.

EXPERIMENTAL EQUIPMENT

In this study, 90 samples of virgin PET in pelletized form with different intrinsic viscosity, diethylene glycol, isophthalic acid, and carboxyl end group values were measured with an OMNIS NIR Analyzer Solid (Figure 1) in diffuse reflection mode (1000–2250 nm) using a large cup OMNIS NIR, 100 mm and large holder OMNIS NIR, 100 mm. To compensate for the inhomogeneity of the samples, rotation and multipoint measurement was used.

Additionally, 50 samples of recycled PET pellets and 200 samples of recycled PET flakes were measured under the same conditions as previously mentioned.

All data acquisition and prediction model development was performed with OMNIS Software.



Figure 1. OMNIS NIR Analyzer Solid with large cup OMNIS NIR and polymer sample.

RESULT

The near-infrared spectra of virgin PET and recycled PET (Figures 2–4), along with the corresponding reference values, were used to create prediction models for quantification of all the quality control parameters listed earlier.

The quality of the prediction models was evaluated using correlation diagrams (Figures 5–10) which display the relation between the NIR prediction and the reference values of intrinsic viscosity, carboxyl end group, isophthalic acid, and diethylene glycol content using different analytical methods. The respective figures of merit (FOM) display the expected precision during routine analysis.

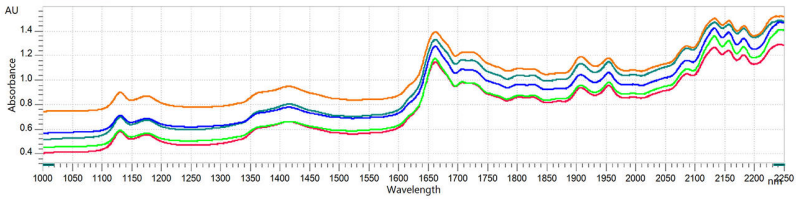

Figure 2. Selection of NIR spectra of virgin PET samples in pellet form. Data was obtained with an OMNIS NIR Analyzer Solid.

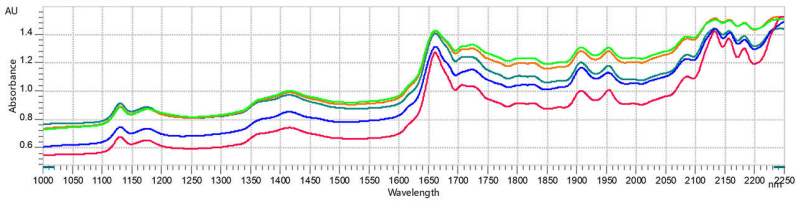

Figure 3. Selection of NIR spectra of recycled PET samples in pellet form. Data was obtained with an OMNIS NIR Analyzer Solid.

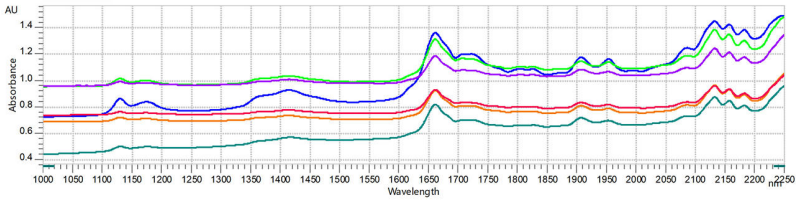

Figure 4. Selection of NIR spectra of recycled PET samples in flake form. Data was obtained with an OMNIS NIR Analyzer Solid.

RESULT INTRINSIC VISCOSITY IN VIRGIN PET

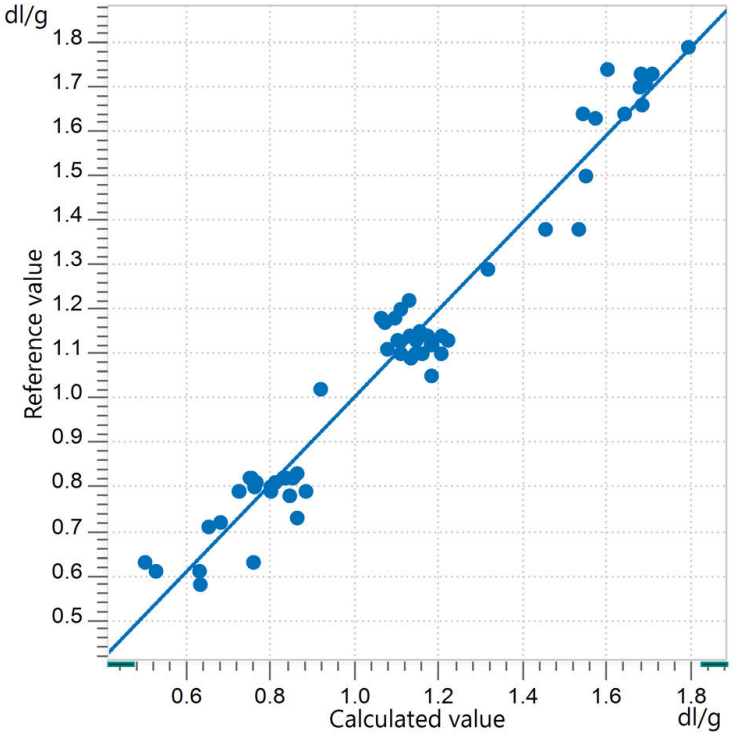

Figure 5. Correlation diagram and the respective FOMs for the prediction of intrinsic viscosity in virgin PET pellets using an OMNIS NIR Analyzer Solid.

R^2 CV	SEC (dL/g)	SECV (dL/g)

0.868	1.70	1.75

RESULT ISOPHTHALIC ACID CONTENT IN VIRGIN PET

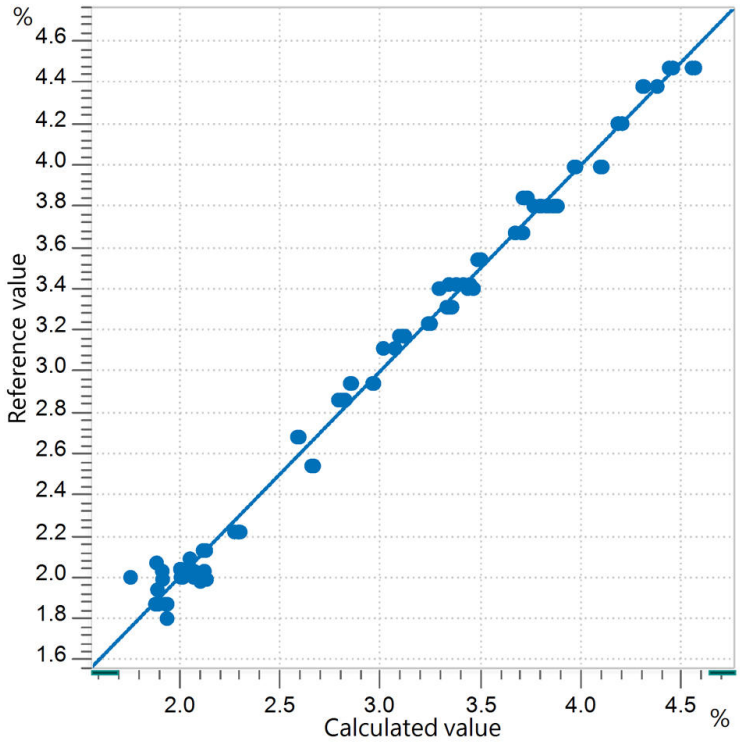

Figure 6. Correlation diagram and the respective FOMs for the prediction of isophthalic acid content in virgin PET pellets using an OMNIS NIR Analyzer Solid. HPLC was the lab method used to determine isophthalic acid in PET.

R^2 CV	SEC (%)	SECV (%)
0.993	0.06	0.07

RESULT DIETHYLENE GLYCOL CONTENT IN VIRGIN PET

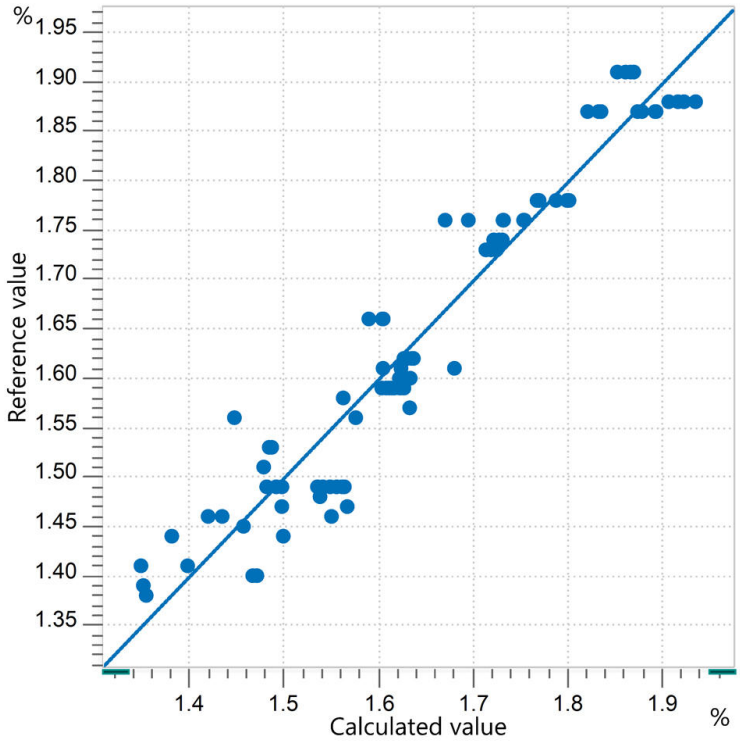

Figure 7. Correlation diagram and the respective FOMs for the prediction of diethylene glycol content in virgin PET pellets using an OMNIS NIR Analyzer Solid. The lab method used for diethylene glycol content in PET was extraction followed by analysis by HPLC-MS.

R^2 CV	SEC (%)	SECV (%)
0.925	0.04	0.04

RESULT CARBOXYL END GROUP CONTENT IN VIRGIN PET

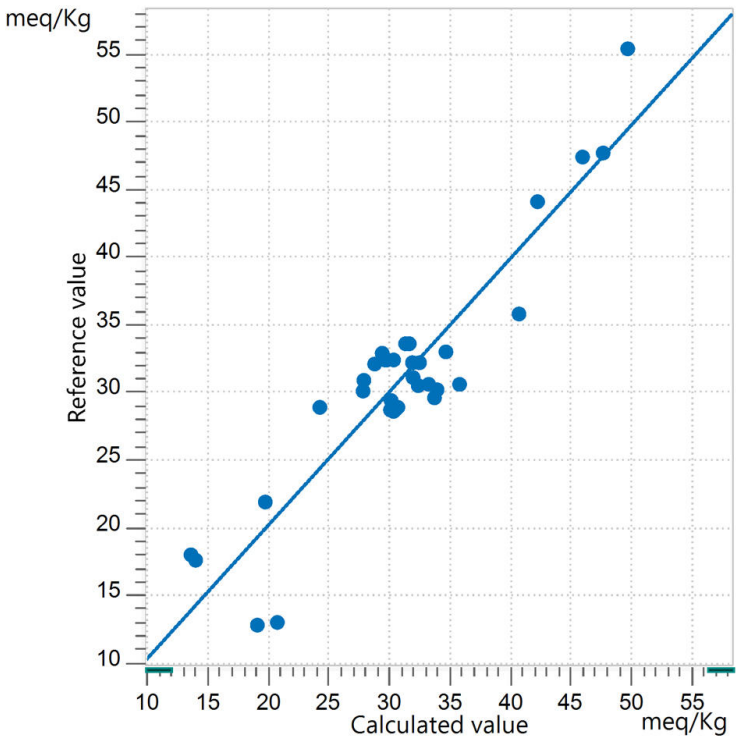

Figure 8. Correlation diagram and the respective FOMs for the prediction of carboxyl end group content in virgin PET pellets using an OMNIS NIR Analyzer Solid. Titration was the lab method used for carboxyl end group analysis of PET.

R^2 CV	SEC (meq/kg)	SECV (meq/kg)
0.852	2.91	3.30

RESULT INTRINSIC VISCOSITY IN RECYCLED PET (PELLET FORM)

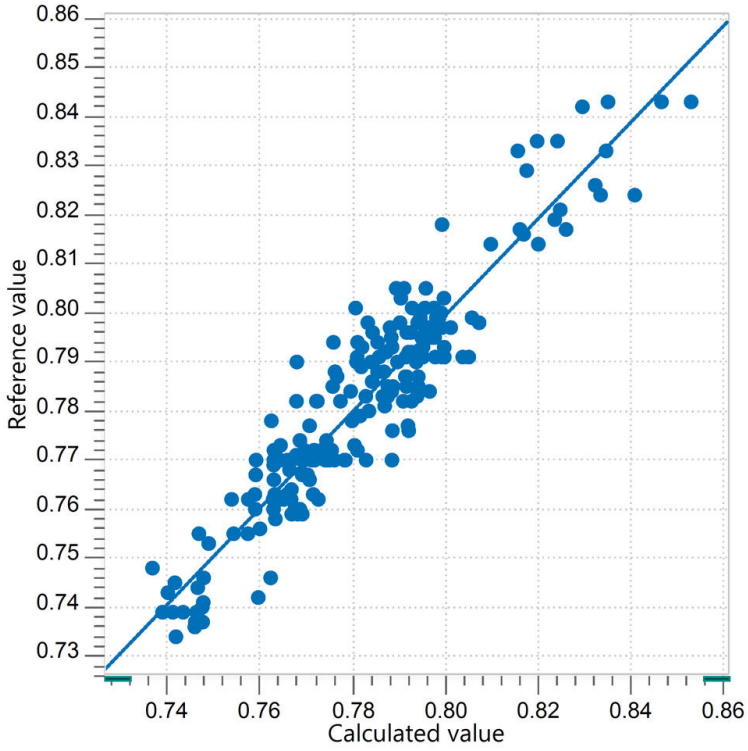

Figure 9. Correlation diagram and the respective FOMs for the prediction of intrinsic viscosity in recycled PET pellets using an OMNIS NIR Analyzer Solid.

R^2 CV	SEC (dL/g)	SECV (dL/g)
0.881	0.0070	0.0079

RESULT INTRINSIC VISCOSITY IN RECYCLED PET (FLAKES FORM)

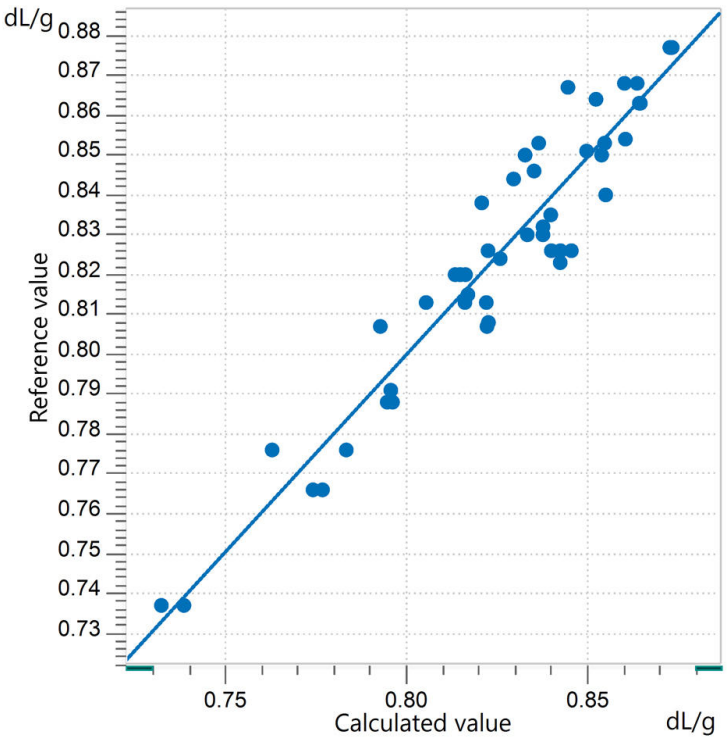

Figure 10. Correlation diagram and the respective FOMs for the prediction of intrinsic viscosity in recycled PET flakes using an OMNIS NIR Analyzer Solid.

R^2 CV	SEC (dL/g)	SECV (dL/g)
0.905	0.0088	0.0102

CONCLUSION

This study demonstrates the feasibility of using NIR spectroscopy for the analysis of key quality parameters of PET. An important benefit of NIR spectroscopy PET analysis is that no sample preparation is required. When compared to wet chemical methods (Table 1), the time to result is a major advantage of NIR spectroscopy, since all parameters are determined in a single measurement in a few seconds.

Table 1. Time to result overview for the different parameters analyzed in this study.

Parameter	Method	Time to result
Diethylene glycol	Extraction + analysis HPLC-MS	45 min (preparation) + 40 min (HPLC)
Isophthalic acid	Dissolve + HPLC	45 min (preparation) + 40 min (HPLC)
Intrinsic viscosity	Dissolve + viscometry	90 min (preparation) + 1 min (viscometry)
Carboxyl end group	Dissolve + titration	90 min (preparation) + 10 min (titration)

CONTACT

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CONFIGURATION



OMNIS NIR Analyzer Solid

Near-infrared spectrometer for solid and viscous samples.

Developed and produced in accordance with Swiss quality standards, the OMNIS NIR Analyzer is the near-infrared spectroscopy (NIRS) solution for routine analysis along the entire production chain. Its application of the latest technologies and its integration in the modern OMNIS Software are reflected in its speed, operability and flexible utilization of this NIR spectrometer.

Overview of the advantages of the OMNIS NIR Analyzer Solid:

- Measurements of solids and viscous samples in less than 10 seconds
- Automated multi-position measurements for reproducible results, even with nonhomogeneous samples
- Simple integration in an automation system or link with additional analysis technologies (titration)
- Supports numerous sample vessels



Large holder OMNIS NIR, 100 mm

Large holder for large sample vessel OMNIS NIR, 100 mm (6.07402.110).

Permits unambiguous positioning of the sample vessel and the rotation of the sample vessel.



Large cup OMNIS NIR, 100 mm

Large sample vessel for the spectra acquisition of powders and granulates in reflection at various sample positions.

The glass bottom is made of resistant Gorilla® Glass.

Compatible with:

- Large holder OMNIS NIR, 100 mm (6.07402.100)

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A WHOLE NEW LEVEL OF PERFORMANCE

OMNIS Stand-Alone license

Enables stand-alone operation of the OMNIS software on a WindowsTM computer.

Features:

- The license already includes one OMNIS instrument license.
- Must be activated via the Metrohm licensing portal.

OMNIS
A WHOLE NEW LEVEL OF PERFORMANCE

Software license Quant Development

Software license for the creation and editing of quantification models in a stand-alone OMNIS Software installation.