Application Note AN-NIR-130

Multiparameter hops analysis by near-infrared spectroscopy (NIRS)

Rapid determination of alpha acids, beta acids, cohumulone content, total oil content, HSI, and moisture

The quality of hops and hop pellets is vital across the entire brewing supply chain. Traditional methods used for quality control (e.g., titration and HPLC) are highly accurate and widely accepted. They are also time consuming, labor intensive, and dependent on chemical reagents which not only incur ongoing material costs but also require careful handling and proper disposal. Near-infrared spectroscopy (NIRS) offers a compelling alternative when ultra-high precision is not necessary. It enables the rapid analysis of multiple parameters within a minute without using any chemicals. This Application Note outlines the measurement setup and the results of cohumulone, hop oils, and moisture content, the hop storage index (HSI), and hops acids analysis with NIRS.

EXPERIMENTAL EQUIPMENT

More than 500 fresh hop samples and ground hop pellets were analyzed on an OMNIS NIR Analyzer Solid (Figure 1). The samples were added to an OMNIS sample cup and analyzed in diffuse reflection mode. To include sample variety, the sample rotated during measurement to collect spectra from different locations. The automatically averaged spectra were used for model development. Spectra acquisition, model development, and validation were carried out with the OMNIS Software.

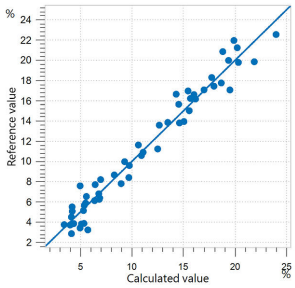
Reference values for alpha acids were obtained using various official methods, including EBC 7.4, EBC 7.5, and EBC 7.7. Total oils and beta acid content were determined using EBC 7.4, while EBC 7.7 was employed for cohumulone analysis. Moisture content and the hop storage index (HSI) were measured using a halogen moisture analyzer and a UV-VIS photometer, respectively.

Figure 1. OMNIS NIR Analyzer Solid.

RESULT

The obtained NIR spectra (Figure 2) were used to create prediction models for the different reference parameters. An external validation set was used to verify the predictive performance of the calculated prediction models if sufficient samples were available. Otherwise an internal cross-validation was conducted. Correlation diagrams which display the relation between the NIR prediction and the reference values are shown in Figures 3–12 together with the respective figures of merit (FOM). For the alpha acid parameter with reference data obtained according to EBC 7.5, a model was created covering the full range (2.40–21.74%). Furthermore, a model for only the lower range (2.43–4.26%) was created to highlight the possibility of reducing the prediction error by creating sub-models for narrower concentration ranges.

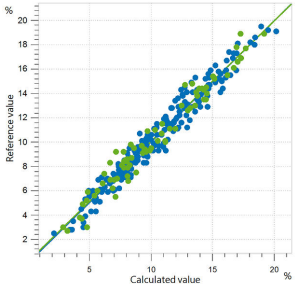
Result alpha acid (EBC 7.4) in fresh hops



Figures of Merit	Value
R2	0.964
Standard Error of Calibration	0.85%
Standard Error of Cross-Validation	1.14%

Figure 3. Correlation diagram and the respective FOMs for the prediction of alpha acid content in hops following the EBC 7.4 norm using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples.

Result alpha acid (EBC 7.5) in fresh hops

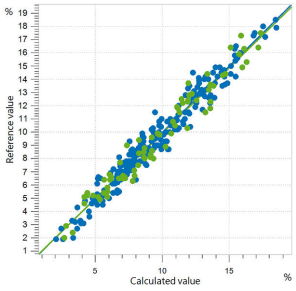


Figures of Merit	Value
R2	0.960
Standard Error of Calibration	0.68%
Standard Error of Cross-Validation	0.74%
Standard Error of Prediction	0.80%

Figure 4. Correlation diagram and the respective FOMs for the prediction of alpha acid content in fresh hops following the EBC 7.5 norm using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples, green dots represent samples used to validate the model.

RESULT

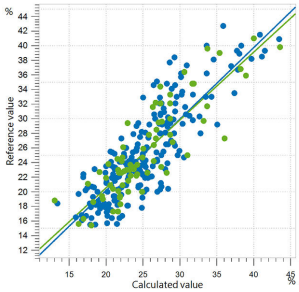
Result alpha acid (EBC 7.7) in fresh hops



Figures of Merit	Value
R2	0.955
Standard Error of Calibration	0.69%
Standard Error of Cross-Validation	0.73%
Standard Error of Prediction	0.81%

Figure 5. Correlation diagram and the respective FOMs for the prediction of alpha acid content in fresh hops following the EBC 7.7 norm using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples, green dots represent samples used to validate the model.

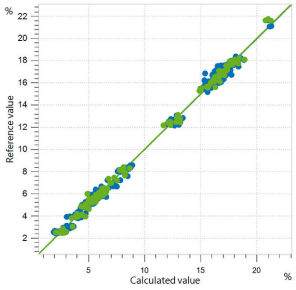
Result cohumulone in fresh hops



Figures of Merit	Value
R2	0.726
Standard Error of Calibration	3.01%
Standard Error of Cross-Validation	3.29%
Standard Error of Prediction	3.27%

Figure 6. Correlation diagram and the respective FOMs for the prediction of cohumulone content in fresh hops following the EBC 7.7 norm using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples, green dots represent samples used to validate the model.

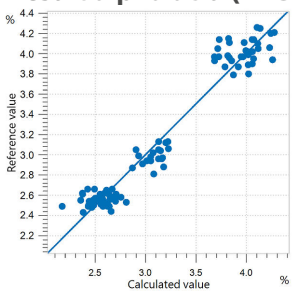
Result alpha acid (EBC 7.5) in ground hop pellets – full concentration range



Figures of Merit	Value
R2	0.997
Standard Error of Calibration	0.32%
Standard Error of Cross-Validation	0.35%
Standard Error of Prediction	0.32%

Figure 7. Correlation diagram and the respective FOMs for the prediction of alpha acid content in ground hop pellets following the EBC 7.5 norm using an OMNIS NIR Analyzer Solid over the full concentration range (2.40–21.74%). Blue dots represent calibration samples, green dots represent samples used to validate the model.

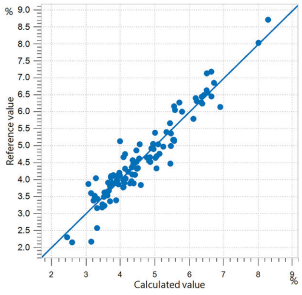
Result alpha acid (EBC 7.5) in ground hop pellets – lower concentration range



Figures of Merit	Value
R2	0.948
Standard Error of Calibration	0.09%
Standard Error of Cross-Validation	0.15%

Figure 8. Correlation diagram and the respective FOMs for the prediction of alpha acid content in ground hop pellets following the EBC 7.5 norm using an OMNIS NIR Analyzer Solid over a lower concentration range (2.43–4.26%). Blue dots represent calibration samples.

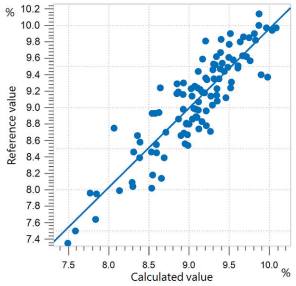
Result beta acid in ground hop pellets



Figures of Merit	Value
R2	0.907
Standard Error of Calibration	0.34%
Standard Error of Cross-Validation	0.37%

Figure 9. Correlation diagram and the respective FOMs for the prediction of beta acid content in ground hop pellets following the EBC 7.4 norm using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples.

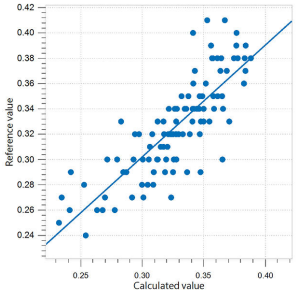
Result total oil content in ground hop pellets



Figures of Merit	Value
R2	0.793
Standard Error of Calibration	0.22%
Standard Error of Cross-Validation	0.27%

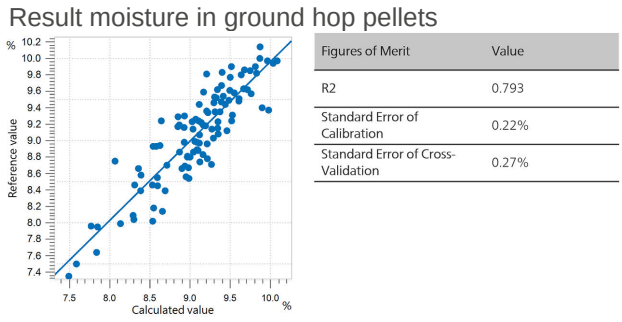
Figure 10. Correlation diagram and the respective FOMs for the prediction of total oil content in ground hop pellets following the EBC 7.4 norm using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples.

Result HSI in ground hop pellets



Figures of Merit	Value
R2	0.669
Standard Error of Calibration	0.015%
Standard Error of Cross-Validation	0.022%

Figure 11. Correlation diagram and the respective FOMs for the prediction of hop storage index in ground hop pellets using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples. Reference values were obtained with a UV-VIS photometer.



Figures of Merit	Value
R2	0.793
Standard Error of Calibration	0.22%
Standard Error of Cross-Validation	0.27%

Figure 12. Correlation diagram and the respective FOMs for the prediction of moisture in ground hop pellets using an OMNIS NIR Analyzer Solid. Blue dots represent calibration samples. Reference values were obtained with a halogen moisture analyzer.

CONCLUSION

This Application Note demonstrates the feasibility of using NIR spectroscopy for the analysis of freshly harvested hops and ground hop pellets to determine cohumulone, moisture, and total oil content, HSI, and alpha and beta acids.

Using alpha acids as an example, the difference between a prediction model covering the full concentration range and a model specific to a narrower range was highlighted. The latter reduced the prediction error by a factor of two. Users can apply this approach to maximize accuracy. In the OMNIS Software, both models can be combined to automatically perform the following sequence. First, the alpha acid concentration is estimated using the broad-range model; then, a more precise prediction is made using the restricted-range model.

Since NIRS measurements are rapid and require no chemicals, the method offers significant time- and cost-savings, as shown in **Table 1**.

Furthermore, the simplicity of the analysis and the availability of a pre-calibrated instrument, using the **pre-calibration, hops, solid** (6.06008.022), make both the implementation and the application of NIR spectroscopy with OMNIS NIRS straightforward.

Table 1. Overview of time effort and costs for the analysis of different parameters in hops by traditional methods and NIR spectroscopy.

Parameter	Method	Estimated time (with sample preparation)	Estimated costs (chemicals, consumables)
Alpha acids	Titration	50 min	$5
Beta acids	HPLC	25 min	$10
Cohumulone	HPLC	(part of beta acid analysis)	(part of beta acid analysis)
Total oil content	Steam distillation	190 min	$5
HSI	UV-VIS	45 min	$5
Moisture	Halogen drier	7 min	$0
All parameters	**NIR spectroscopy**	**2 min**	**$0**

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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

Small holder OMNIS NIR, 60 mm

Small holder for small sample vessel OMNIS NIR, 60 mm (6.07402.210).

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

Small cup OMNIS NIR, 60 mm

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

Compatible with:

- Small holder OMNIS NIR, 60 mm (**6.07402.200**)

OMNIS
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.
- Not transferable to another computer.

OMNIS
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Software license Quant Development

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

Pre-calibration, hops, solid

OMNIS pre-calibration for determination of moisture, the Hop Storage Index HSITHC, and the alpha acid and beta acid content in hops using NIR spectroscopy.