Application Note AN-NIR-107

Quality control of Bromobutyl rubber

Multiparameter determination within one minute using NIRS

Products made from either natural or synthetic rubber are a vital part of everyday living. Synthetic rubbers offer superior thermal stability and resistance to oxidizing agents and oils. One synthetic rubber uses Bromobutyl (BIIR), a copolymer of isobutylene and small amounts of brominated isoprene that provides unsaturated vulcanization sites. Bromobutyl rubber is derived from halogenating butyl rubber with bromine in a continuous process. This elastomer has many of the attributes of butyl rubber, but the addition of bromine improves adhesion to other rubbers and metals, resulting in substantially faster cure rates (i.e., lower amounts of curative agents are required).
Usually, the determination of the bromine content and other quality parameters (e.g., Mooney viscosity, volatile content, calcium stearate content, and functional bromide) requires various reagents and time-consuming analytical methods. However, near-infrared spectroscopy (NIRS) offers rapid and reliable simultaneous quantification of those parameters in Bromobutyl rubber without the use of chemicals.

A total of 68 samples of Bromo Isobutylene Isoprene rubber (BIIR, Bromobutyl rubber) were collected to create a prediction model for quantification of several quality control parameters including Mooney viscosity, bromine content, volatile matter content, calcium stearate content, and functional bromide. All samples were measured with a Metrohm NIRS DS2500 Liquid Analyzer (400–2500 nm, **Figure 1**) in transmission mode with an 8 mm sample holder. Reproducible spectrum acquisition was achieved using the built-in temperature control set at 50 °C. For convenience, disposable vials with a pathlength of 8 mm were used, which made cleaning of the sample vessels unnecessary. The Metrohm software package Vision Air Complete was used for all data acquisition and prediction model development.

Table 1. Hardware and software equipment overview.

Equipment	Article number
DS2500 Liquid Analyzer	2.929.0010
DS2500 Holder 8 mm vials	6.749.2020
Disposable vials, 8 mm	6.7402.000
Vision Air 2.0 Complete	6.6072.208

Figure 1. Metrohm NIRS DS2500 Liquid Analyzer used for the quantification of several QC parameters in BIIR samples.

All measured Vis-NIR spectra (Figure 2) were used to create a prediction model for quantification of the key quality parameters of BIIR. The quality of the prediction model was evaluated using correlation diagrams which display a very high correlation between the Vis-NIR prediction and the reference values. The respective figures of merit (FOM) display the expected precision of a prediction during routine analysis (Figures 3–7).

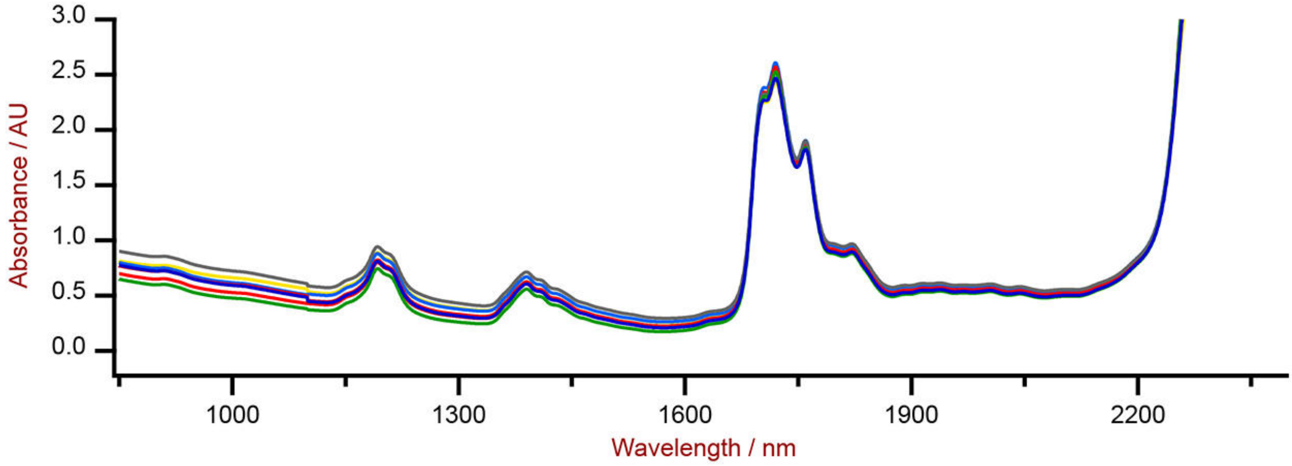

Figure 2. Selection of Vis-NIR spectra of several BIIR samples analyzed on a DS2500 Liquid Analyzer with disposable 8 mm vials.

RESULT MOONEY VISCOSITY

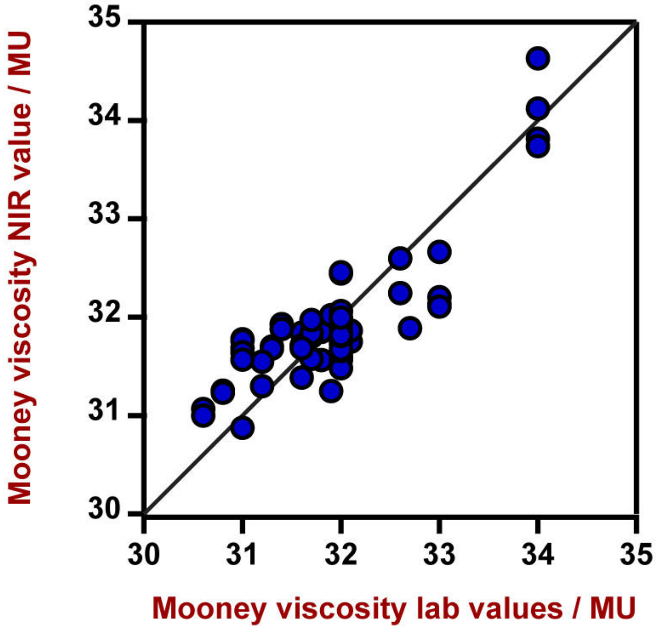

Figure 3. Correlation diagram and the respective figures of merit for the prediction of Mooney viscosity in BIIR using a DS2500 Liquid Analyzer. The lab values were evaluated using a Mooney viscometer.

Figures of Merit	Value
R^2	0.7257
Standard Error of Calibration	0.442 %
Standard Error of Cross-Validation	0.614 %

RESULT BROMINE CONTENT

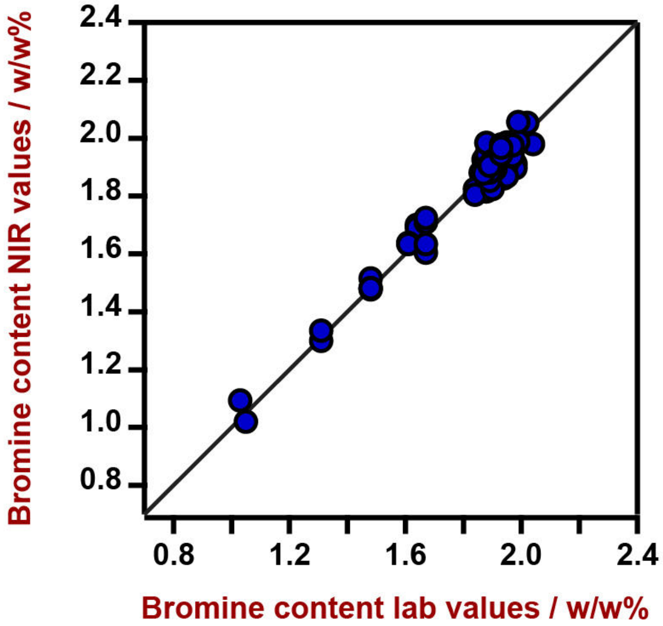

Figure 4. Correlation diagram and the respective figures of merit for the prediction of bromine content in BIIR using a DS2500 Liquid Analyzer. The lab values were evaluated by titration.

Figures of Merit	Value
R^2	0.9629
Standard Error of Calibration	0.046 %
Standard Error of Cross-Validation	0.064 %

RESULT VOLATILE CONTENT

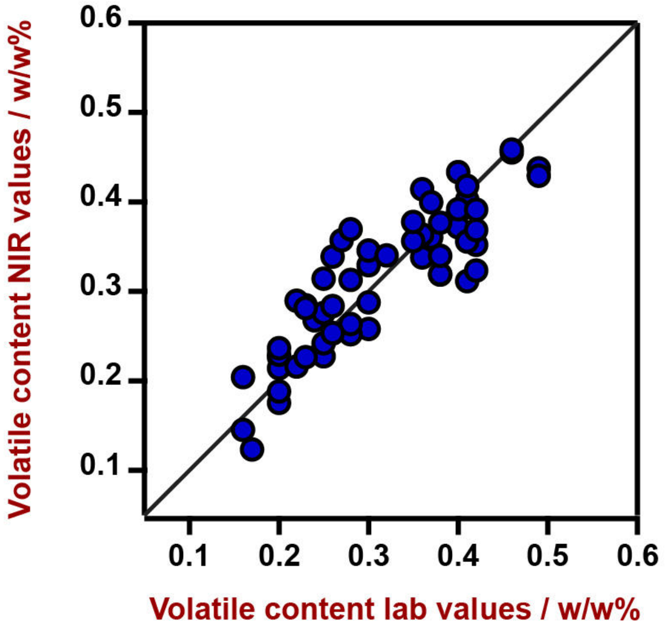

Figure 5. Correlation diagram and the respective figures of merit for the prediction of volatile matter content in BIIR using a DS2500 Liquid Analyzer. The lab values were evaluated by an oven method.

Figures of Merit	Value
R^2	0.7730
Standard Error of Calibration	0.046 %
Standard Error of Cross-Validation	0.056 %

RESULT CALCIUM STEARATE CONTENT

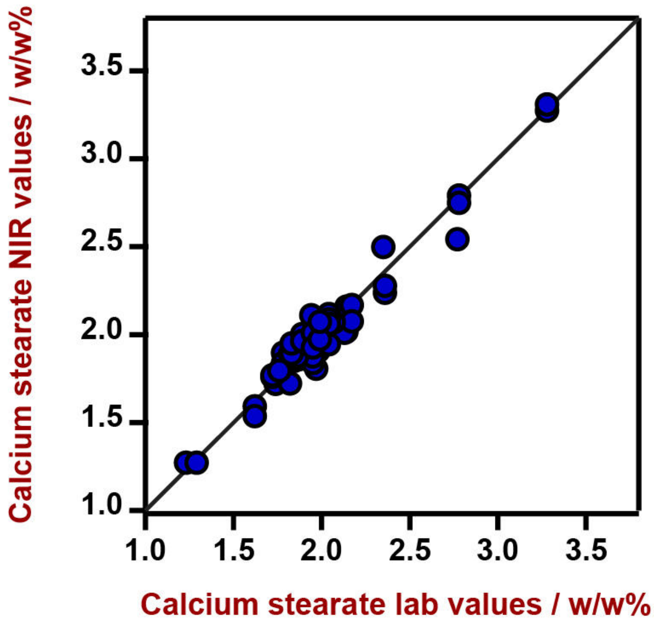

Figure 6. Correlation diagram and the respective figures of merit for the prediction of calcium stearate content in BIIR using a DS2500 Liquid Analyzer. The lab values were evaluated by an X-Ray fluorescence (XRF) spectrometer.

Figures of Merit	Value
R^2	0.9541
Standard Error of Calibration	0.082 %
Standard Error of Cross-Validation	0.153 %

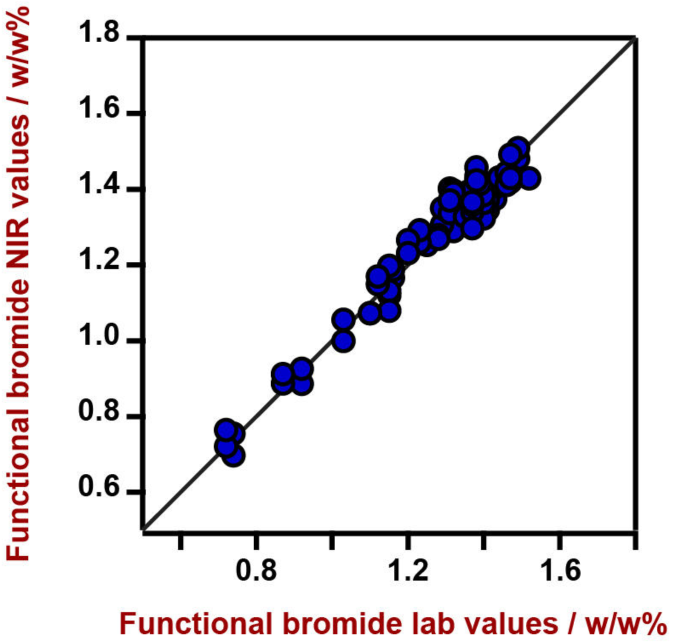

Figure 7. Correlation diagram and the respective figures of merit for the prediction of functional bromide content in BIIR using a DS2500 Liquid Analyzer. The lab values were evaluated by Nuclear Magnetic Resonance (NMR).

Figures of Merit	Value
R^2	0.958
Standard Error of Calibration	0.044 %
Standard Error of Cross-Validation	0.060 %

This Application Note demonstrates the feasibility to determine multiple key parameters for the quality control of Bromobutyl rubber with NIR spectroscopy. Vis-NIR spectroscopy enables a fast alternative with high accuracy, and therefore represents a suitable alternative to the standard methods (Table 2). No chemicals are required with near-infrared spectroscopic analysis, and cleanup is quick and easy when using disposable sample vials as shown in this study.

Table 2. Time to result overview for the quantification of different QC parameters in BIIR.

Parameter	Method	Time to result
Mooney viscosity	Mooney viscometer	5 min (prep.) + 5 min (Gas Chromatography)
Volatile content	Oven method	5 min
Bromine content	Titration	5 min
Calcium stearate	X-Ray fluorescence spectrometer	5 min
Functional bromide	Nuclear Magnetic Resonance	24 hours (dissolve) + ~2 min (NMR)

CONCLUSION

Internal reference: AW NIR CN-0019-112022

CONTACT

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CONFIGURATION

DS2500 Liquid Analyzer

Robust near-infrared spectroscopy for quality control, not only in laboratories but also in production environments.

The DS2500 Liquid Analyzer is the tried and tested, flexible solution for routine analysis of liquids along the entire production chain. Its robust design makes the DS2500 Liquid Analyzer resistant to dust, moisture and vibrations, which means that it is eminently suited for use in harsh production environments.

The DS2500 Liquid Analyzer covers the full spectral range from 400 to 2500 nm, heats samples up to 80°C and is compatible with various disposable vials and quartz cuvettes. The DS2500 Liquid Analyzer is thus adaptable to your individual sample requirements and helps you obtain accurate and reproducible results in less than one minute. The integrated sample holder detection and the self-explanatory Vision Air Software also ensure simple and safe operation by the user.

In the case of larger-sized sample quantities, productivity can be considerably increased by using a flow-through cell in combination with a Metrohm sample robot.