Mid-infrared versus near-infrared spectroscopy: a case study of the quality control of bitumen

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The rapid quantitative analysis of additives in bitumen is an important issue for quality control in road construction work. The objective of this study was to compare the prediction performance of PLS calibration models for this purpose based on two vibrational spectroscopic techniques: NIR transmission spectroscopy with a laboratory instrument and FT-IR/ATR (attenuated total reflection) spectroscopy with a hand-held spectrometer. The last-mentioned alternative has the significant advantage that it can readily be applied as an in-situ "on-the-road" method.

Keywords: bitumen, additives, NIR spectroscopy, FT-IR/ATR spectroscopy, PLS calibration.

Introduction

Bitumen is a complex mixture of high-molecular weight hydrocarbons and for application in road construction work it is often blended with different polymers in order to adjust the rheological and adhesional properties.^{1–3} Due to this complex chemical matrix, there are only a few analytical methods available. In the present communication two vibrational spectroscopic techniques are compared with reference to their performance for the quantitative determination of additives in bitumen. These are FT-NIR transmission spectroscopy with a laboratory instrument and FT-IR/ ATR spectroscopy with a hand-held instrument. Specifically, the determination of polypropylene/ maleic anhydride (PPMA) additive in bitumen in the concentration range from 0-5% (w/w) was investigated and in both cases the spectral data were evaluated with chemometric PLS regression routines.

Experimental

Spectrometers and chemometric evaluation software

The NIR transmission measurements were performed on a Bruker IFS 88 FT-spectrometer (Bruker Optik GmbH, Ettlingen, Germany) adapted for the NIR region with a tungsten-halogen

source, a quartz beam splitter, and a liquid-nitrogen cooled InSb detector. Spectra were measured in the 3000–12000 cm⁻¹ wavenumber region by accumulating 64 scans with a spectral resolution of 8 cm⁻¹. The FT-IR/ATR spectrometer (TruDefender) was kindly supplied by Ahura Scientific, Inc. (Wilmington, MA, USA). This instrument is based on a laser referenced interferometer with a ZnSe beamsplitter and a DTGS detector. Spectra were measured with the integrated singlebounce diamond ATR unit in the 650–4000 cm⁻¹ wavenumber region by accumulating 60 scans with a 4 cm⁻¹ spectral resolution. For the NIR transmission measurements bitumen layers with a reproducible thickness of 200 μ m were sandwiched between glass slides. The much simpler FT-IR/ATR measurement with the hand-held instrument of a bitumen sample spot prepared on a glass slide is demonstrated in Figure 1.

With the chemometric software package The Unscrambler® (Version 9.7, Camo Software AS, Oslo, Norway) PLS models⁴ were developed for both data sets and subsequently unknown samples were predicted from their spectra in terms of their PPMA content.

Materials

The bitumen/additive formulations were prepared by admixture of polypropylene/maleic anhydride (Clariant GmbH, Gersthofen, Germany) to MBW 10–25 bitumen (Mitteldeutsches Bitumenwerk, Hoehenmoelsen, Germany) in the concentration range 1–5 % (w/w) by vigorous stirring at 165 °C for 1 h.³



Figure 1. The hand-held FT-IR/ATR spectrometer (Ahura TruDefender) applied for the measurement of bitumen sample spots on a glass slide.



Figure 2. FT-NIR transmission spectra (upper) and FT-IR/ATR spectra (lower) of bitumen/PPMA additive formulations (without data pretreatment).

Results and discussion

Calibrations

A series of different bitumen/additive mixtures with PPMA concentrations in the range 1-5% (w/w) were prepared as calibration sample set. Typical FT-NIR transmission spectra and FT-IR/ATR spectra are shown in Figures 2(a) and 2(b), respectively.

The data pretreatment of the FT-NIR transmission spectra consisted of selecting the wavenumber regions $6202-5530 \text{ cm}^{-1}$ and $5130-4000 \text{ cm}^{-1}$ and applying an extended multiplicative signal correction (EMSC) procedure.⁵ For the FT-IR/ATR spectra the wavenumber regions $3250-2500 \text{ cm}^{-1}$, $1490-1130 \text{ cm}^{-1}$ and $930-680 \text{ cm}^{-1}$ were selected and then a standard normal variate (SNV) transformation was applied. Based on these pre-treated calibration spectra PLS-1 calibration models with full cross-validation were developed. In Table 1 the most important calibration/cross-validation parameters of the optimized PLS-1 calibration models of the two different spectra types are summarised.

Prediction of unknown samples

The spectra of test samples which were not contained in the calibration set and which had been prepared in different time intervals were then predicted with reference to their PPMA additive content with the calibration models outlined in Table 1.

PLS-1 calibration with FT-NIR/transmission spectra				
Parameter	Calibration	Cross-validation		
Slope	0.999049	0.999440		
Offset	0.002144	-0.003756		
Correlation	0.999524	0.999415		
RMSEC/RMSEP	0.059226	0.065891		
SEC/SEP	0.060500	0.067113		
PLS-1 calibration with FT-IR/ATR spectra				
PLS-1 cali	bration with FT-IR/ATR	spectra		
PLS-1 cali Parameter	bration with FT-IR/ATR Calibration	spectra Cross-validation		
PLS-1 cali Parameter Slope	bration with FT-IR/ATR Calibration 0.976419	spectra Cross-validation 0.964531		
PLS-1 cali Parameter Slope Offset	bration with FT-IR/ATR Calibration 0.976419 0.060637	spectra Cross-validation 0.964531 0.096279		
PLS-1 cali Parameter Slope Offset Correlation	bration with FT-IR/ATRCalibration0.9764190.0606370.988139	spectra Cross-validation 0.964531 0.096279 0.974496		
PLS-1 cali Parameter Slope Offset Correlation RMSEC/RMSEP	bration with FT-IR/ATR Calibration 0.976419 0.060637 0.988139 0.239291	spectra Cross-validation 0.964531 0.096279 0.974496 0.350533		

 Table 1. PLS-1 calibration/crossvalidation parameters obtained for the FT-NIR transmission and FT-IR/ATR calibration spectra of bitumen/PPMA additive formulations.

FT-NIR/transmission polypropylene/maleic anhydride					
Sample	Prediction	Reference	Δ pred – ref		
	% (w/w)	% (w/w)	% (w/w)		
TMBW 10-25 PPMA2.3/1	2.401	2.300	0.101		
TMBW 10-25 PPMA2.3/2	2.396	2.300	0.096		
TMBW 10-25 PPMA2.3/3	2.358	2.300	0.058		
TMBW 10-25 PPMA2.3/4	2.350	2.300	0.050		
TMBW 10-25 PPMA3.0/1	3.180	3.000	0.180		
TMBW 10-25 PPMA3.0/2	3.159	3.000	0.159		
TMBW 10-25 PPMA4.5/1	4.429	4.500	-0.071		
TMBW 10-25 PPMA4.5/2	4.499	4.500	0.001		
TMBW 10-25 PPMA4.5/3	4.306	4.500	-0.194		
TMBW 10-25 PPMA4.5/4	4.339	4.500	-0.161		

Table 2. Comparison of predicted and reference concentrations of the polypropylene/ maleic anhydride additive for the PLS-1 calibrations based on the FT-NIR transmission and the FT-IR/ATR spectra of samples not contained in the calibration set.

FT-IR/ATR	FT-IR/ATR polypropylene/maleic anhydride				
Sample	Prediction % (w/w)	Reference % (w/w)	Δ pred – ref % (w/w)		
AMBW 10-25 PPMA2.3/1	2.424	2.300	0.124		
AMBW 10-25 PPMA2.3/2	2.536	2.300	0.236		
AMBW 10-25 PPMA2.3/3	1.849	2.300	0.451		
AMBW 10-25 PPMA2.3/4	2.460	2.300	0.160		
AMBW 10-25 PPMA3.0/1	3.023	3.000	0.023		
AMBW 10-25 PPMA3.0/2	3.440	3.000	0.440		
AMBW 10-25 PPMA4.5/1	4.308	4.500	-0.192		
AMBW 10-25 PPMA4.5/2	4.787	4.500	0.287		
AMBW 10-25 PPMA4.5/3	4.251	4.500	-0.249		
AMBW 10-25 PPMA4.5/4	4.506	4.500	0.006		

In Table 2 the predicted values are compared to the corresponding reference values, and demonstrate the achievable prediction accuracy.

Laboratory-based FT-NIR transmission technique provided models which yielded a somewhat higher prediction accuracy compared to the FT-IR/ATR spectra, recorded with the hand-held

instrument. Nevertheless, it has to be emphasised that the sample preparation for the NIR transmission technique is much more time consuming, and the disadvantage of a slightly higher prediction error of the FT-IR/ATR measurement is more than compensated for by the flexibility of its in-situ applicability.

Conclusions

The performance of FT-NIR transmission spectroscopy for the quantitative determination of the bitumen additive polypropylene/maleic anhydride was compared to FT-IR/ATR measurements operated with a miniaturized hand-held spectrometer. With both techniques an acceptable prediction accuracy was achieved with some advantages for the FT-NIR transmission technique. Nevertheless, the hand-held system is the preferable alternative for this analytical application due to the lack of sample preparation and primarily due to its flexible use as in-situ technique at road construction sites.

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