Abstract
Feasibility study of improving accuracy of near infrared measurement for highly complex mixtures using multiple backgrounds

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Introduction

Near-Infrared (NIR) spectroscopy has been widely applied and utilised as an efficient analytical method in diverse fields, because it is fast, simple and non-destructive, and requires no chemical reagents. The most significant drawback of NIR spectroscopy is associated with low spectral selectivity and sensitivity, due to the nature of overtone and combination bands. When an analysis for samples with a simple chemical matrix is targeted using NIR spectroscopy, the spectral selectivity would not be a critical issue. On the contrary, it will become more crucial if samples are highly complex mixtures such as lube base oil, one of the most popular petroleum-driven products. In this situation, a practical approach to overcome the inferior spectral selectivity would be the determination of an optimal spectral region for multivariate calibration, using techniques such as moving window partial least squares (MWPLS) and interval PLS (IPLS). Since NIR spectral selectivity is quite limited, the optimal selection of spectral ranges has helped to improve accuracy of compositional analysis marginally. Alternatively, we have proposed the method of improving the accuracy of properties of lube base oil by improving spectral selectivity, and the strategy is schematically shown in Figure 1.

Along with absorbance spectra using air as a background, other spectra were collected using 4 different hydrocarbons (1,2,4-trimethyl cyclohexane, ethyl benzene, *n*-decane and 2,2,4-trimethylpentane). By this method, five different absorbance spectra could be generated, using five different backgrounds for a given sample. The object of this study was to evaluate possible improvement of accuracy in the determination of lube oil properties, when these five different spectra are optimally used for development of calibration models using a multivariate calibration system, such as partial least squares regression (PLSR).

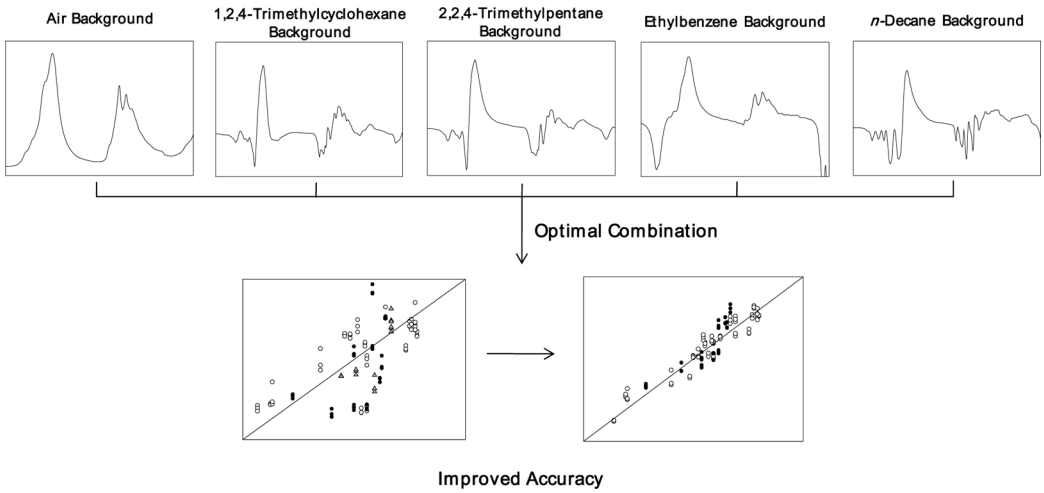

Figure 1. Schematic diagram showing the concept of combining different spectral features obtained from different backgrounds.

Materials and methods

LBO samples were acquired from SK Energy, Korea. All the NIR spectra were collected using an ABB Bomem MB-160 FT-NIR spectrometer equipped with a tungsten-halogen source and InGaAs detector. The vial holder was used to hold a glass vial as well as to control the temperature. The narrow rectangular aperture of 0.85 mm (width) was used to minimise the spectroscopic deviations from the round surface of a vial. NIR spectra were collected over 9500–4500 cm^{-1} range with the resolution of 8 cm^{-1}. As mentioned, NIR spectra of a sample were collected by varying backgrounds (air, 1,2,4-trimethyl cyclohexane, ethyl benzene, *n*-decane and 2,2,4-trimethylpentane).

Results and discussion

With the use of PLS, we initially determined the properties of lube oil using each spectral dataset obtained from each background. This was to evaluate the variation of accuracies when different backgrounds were used. Then, we evaluated the resulting PLS accuracies when these spectra were combined. When a background is changed to obtain absorbance spectra, the spectral features related to the property change should show different characteristics. Consequently, the optimal combination of different spectral features could lead to improved accuracy for the determination of relevant properties.