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Inline Monitoring of Butane Isomers Adsorption on MFI Using Near-Infrared Spectroscopy: Drift Correction in Time Based Experiments

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Near-infrared (NIR) spectroscopy is used to monitor online a large variety of processes. Hydrocarbons with their strong NIR spectral signature are good candidate analytes. For this work, the sorption data are measured in a manometric setup coupled with online NIR spectroscopy, to monitor the bulk composition. The assessment of time based results faces a baseline stability problem. The goal of this article is to study the robustness of different spectral preprocessing methods when dealing with time based data. In this study, it was found that for time based experiments it is necessary to perform drift correction on the spectra combined with a water band correction. For the calibration experiments, which only last few seconds, offset correction and drift correction performed equally well.

Introduction

New gasoline specifications demand a lower amount of olefins and aromatics in gasoline. Consequently, there is a greater need in the petroleum industry for catalytic isomerization to convert straight chain hydrocarbons to branched hydrocarbons.¹ Branched hydrocarbons are preferred as ingredients in petrol because they enhance the fuel octane number. Then the separation of linear and branched hydrocarbons becomes necessary. Improving and optimizing such a separation is a problem with growing industrial importance. A variety of zeolites may be used for the separation process. These zeolites can be selected either on the basis of their sorption thermodynamics² or of their sorption kinetics.³ Equilibrium and kinetic data are therefore essential for the development of sorption based separation methods. These data provide also key information regarding the catalytic isomerization on zeolites themselves.

The objective of this project is to measure adsorption properties of mixtures of isomers. We are interested in equilibrium data as well as in kinetics. For that we need a fast in-line analytical technique that allows us to quantify the isomers in the mixture. An in-line technique is necessary because our system operates in gas phase. Off-line techniques (like gas chromatography) are not suitable, since they require that samples be “taken out” and such procedure would change the adsorption process and disturb the equilibrium results. We need a fast technique due to the fact that adsorption can be a very fast process for some adsorptive/adsorbent systems. Spectroscopy is the most suitable tool to get the desired information.

Therefore, we use a manometric setup coupled with a near-infrared (NIR) spectrometer. NIR spectroscopy is a fast, nonintrusive technique that allows us to measure the gas-phase composition without interfering with the adsorption.

To collect the adsorption kinetic data, we perform time based experiments that can take a few hours. Instability of the spectral background will then limit the accuracy of the method since we cannot record background spectra during the experiment. This may give rise to a drift of the spectral baseline. Therefore, a careful data pretreatment is necessary since different data preprocessing might influence the final results. In this paper, we present a comparative study of three different data preprocessing, offset correction, drift correction, and drift correction combined with correction of water bands. The calibration model is “bi-linear” and has two independent sets of parameters, one for the low-pressure region and one for the high-pressure region. The influence of the different preprocessing methods on the calibration model is expected to be small due to the fact that background spectrum and the calibration spectra are collected within a short period from each other. On the other hand, the influence on the time based experiments results is expected to be larger, and is expected to increase proportionally with the difference between the environmental conditions of background and measurement.

Theory

The NIR region (15 000–4000 cm⁻¹) is the region between infrared and the visible light region. NIR absorption spectra correspond to overtone and combination modes of fundamental vibrations.⁴ Therefore, in the NIR region, absorption is weak allowing the gas composition to be measured at high pressures. The vibrational overtone and combination bands that give rise to absorp-

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tion in the near-infrared range can be ascribed mainly to functional groups that contain a hydrogen atom (e.g., OH, CH, NH).⁵ The broad complex bands present in the NIR region are the result of overlapping bands. Therefore, a multivariate analysis is required.

Many economic factors are directly affected by the hydrocarbon composition. There are several applications of NIR spectroscopy related with hydrocarbon processes such as monitoring of the composition and BTU content of natural gas on-line, analyses of the monocyclic aromatic components in gasoline, octane rating of gasoline, and determination of gas-oil ratio for crude oil.^{4,6} Boelens et al.⁷ showed that it is possible to perform fast and accurate analysis of *n*-alkanes in gaseous mixtures of linear, branched and cyclic alkanes with use of NIR spectroscopy.

Calibration Model. To relate the NIR absorbance spectrum of a sample to the amount of alkane in the sample one needs a calibration model. When a univariate spectral quantity (*y*) of some calibration samples was plotted as a function of the pressure (*P*), it could be observed that two different linear regions exist, and thus a "bilinear" model was required. To ensure that the model represents an injective function, a transition pressure parameter (*P_C*) is introduced to indicate where transition occurs of one region to the other region of the model. The model equations are

If $P < P_C$ (low pressures region, LP)

$$y = \alpha_L P + \beta_L \quad (1)$$

If $P \geq P_C$ (high pressures region, HP)

$$y = \alpha_H P + \beta_H \quad (2)$$

If each calibration spectrum is represented by a vector *s*, then *y* is the Euclidean norm of the vector *s* for the single component case. In the multicomponent case *y* is a corrected spectral quantity, as it is presented in the next section. The model has 4 parameters α_L , β_L , α_H , and β_H that are determined by independent linear regression on each region.

Net Analyte Signal Theory (NAS). With the variation of environment humidity during a time based experiment, water bands can appear that might cause problems in the analysis of the spectra. NAS theory can be used to perform the correction for the presence of such water bands in the spectra.

As presented by Lorber,⁸ the net analyte signal of a certain analyte may be computed as the part of its spectrum orthogonal to the contribution of other coexisting constituents. The analyte spectrum *s* (*n* × 1) can always be decomposed into *s[⊥]* and *s⁼*

$$s = s^\perp + s^= \quad (3)$$

where *s⁼* is the part of the analyte spectrum that is not orthogonal to the interferent and is a linear combination of pure interferent spectra. Only the orthogonal part, *s[⊥]* is unique for the sought for analyte and can be computed by⁸

$$s^\perp = (I - WW^+)s \quad (4)$$

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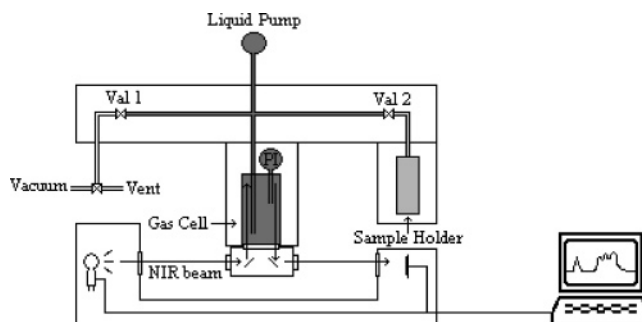


Figure 1. Scheme of the manometric apparatus coupled with the NIR spectrometer.

Table 1. Preprocessing Methods

method	description
none	no preprocessing of spectra
OffSet	offset preprocessing, the offset value is calculated using the interval of [6400; 6475] cm^{-1} for the first region, and [7600; 7750] cm^{-1} for the second region
Drift	correction of baseline with a 1st order polynomial, the intervals to compute the baseline are [6400; 6475] and [7600; 7750] for the first region; [7600; 7750] and [9000; 9200] for the second region
Drift-WB	correction of baseline followed by a water-band correction using NAS approach

where *I* (*n* × *n*) is the identity matrix, and *W* is the interferents matrix, with spectra of interferents on its columns, and *W⁺* is a generalized inverse of *W*. In the present case, *W* is a vector representing the water band spectrum of dimension (*n* × 1). Further information about NAS theory can be found in the literature.^{8–10}

For the calibration model in multicomponent cases only, the Euclidean norm of *s[⊥]* is used to compute *y*.

Experimental Section

Experimental Apparatus. Figure 1 shows the experimental setup. An in-house constructed manometric apparatus coupled with a NIR spectrometer (Perkin-Elmer, FT-IR system, GX Spectrum) was used. Valve *Val 1* (valves 1 and 2 are type SS-HBS4-C, from Nupro Company, Willoughby, OH) enables the introduction of the gas (from Vent) or evacuation of the system (to Vacuum). A Liquid Pump (type P125V125, from Williams Company Inc., Santa Clarita, CA) is used to feed the system when vapors are used. Valve *Val 2* allows isolation of the sample of zeolite in the Sample Holder when feeding or evacuating the gas cell. The pressure transducer PI (XTEL – 190M – 17 BarA, from Kulite Benelux B. V., Den Haag, The Netherlands) monitors the gas cell pressure. The volume of the gas cell chamber is 204 cm^3 , and the sample holder chamber has a volume of 24.4 cm^3 .

Materials. Commercially available MFI from Zeolyst (Zeolyst International, A Partnership of PQ Corporation and CRI Zeolites, Inc., Kansas City, KS) was used as adsorbent material, with a silicon aluminum ratio (Si/Al) of 100, and the crystals do not have a regular shape. The sample was calcined for 6 h at 873 K. The mass of the used sample was of 4.05 g and was cleaned at 573 K during a minimum of 3 h under a vacuum lower than 8×10^{-6} mbar. The adsorptive gases used were *n*-butane with a 99.5% purity and *i*-butane with 99.95% purity from Praxair (Praxair N. V., Oevel, Belgium). These gases were used without any further pretreatment.

Experimental Procedure. For single and multicomponent calibration models, NIR spectra (average of 10 scans with 4 cm^{-1}

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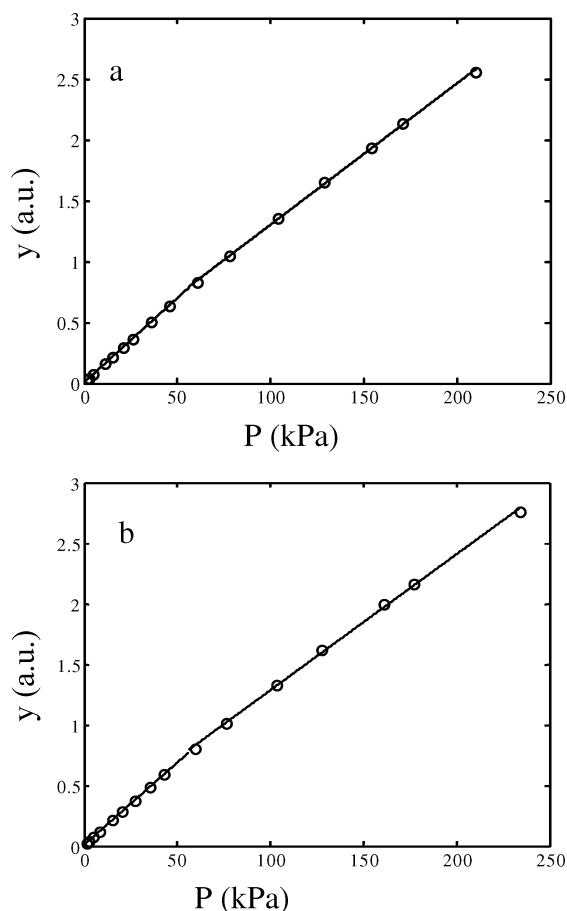


Figure 2. Calibration lines for (a) *n*-butane and (b) isobutane at 373 K using Drift correction.

Table 2. Residual Standard Deviation for *i*- and *n*-butane Calibration for $P < P_C$

RSD in LP (a.u.)	<i>i</i> -butane	<i>n</i> -butane
Off Set	2.8×10^{-3}	4.8×10^{-3}
Drift	1.7×10^{-3}	9.6×10^{-4}
Drift – WB	1.1×10^{-3}	6.2×10^{-4}

Table 3. Residual Standard Deviation for *i*- and *n*-Butane Calibration for $P \geq P_C$

RSD in HP (a.u.)	<i>i</i> -butane	<i>n</i> -butane
Off Set	2.1×10^{-2}	1.5×10^{-2}
Drift	2.2×10^{-2}	1.4×10^{-2}
Drift – WB	1.5×10^{-2}	9.8×10^{-3}

of resolution) of pure gases are recorded at 373 K for several pressures. The data are treated as explained in the Results section.

All sorption experiments were done at 373 K. To perform an adsorption experiment, gas (or vapor) is fed into the gas cell while closing valve 2 in order to isolate the sample. After introduction, valves 1 and 2 are kept closed during the initial period, keeping the pressure constant at its initial value. Spectral data acquisition is started during this initial period. When valve 2 is opened, the adsorption process starts, at this moment a pressure drop is observed. Spectra are recorded in time, so the adsorption uptake can be computed as a function of time. This procedure is repeated to obtain a full adsorption isotherm. Desorption is performed in a similar way. The zeolite is preloaded (by an adsorption step) and then valve 2 is closed to keep the sample isolated. Valve 1 is open to evacuate the system, when maximum vacuum is achieved valve 1 is closed. While the pressure is kept constant at 0 kPa, the recording of spectra is started. Valve 2 is opened after a few minutes and desorption starts until pressure achieves its equilibrium value.

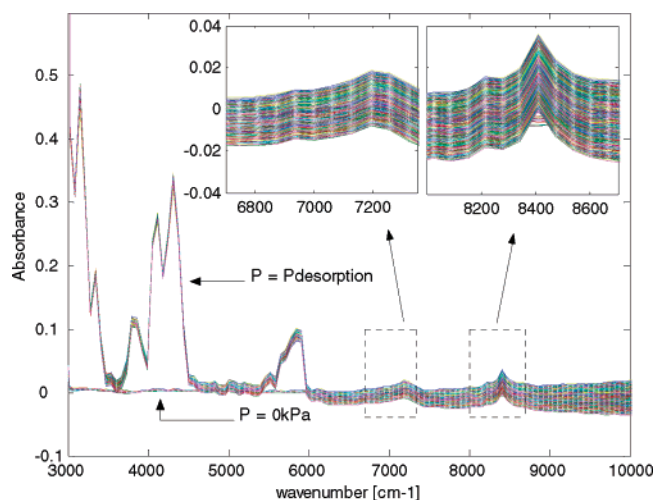


Figure 3. Spectra of desorption experiment, *n*-butane on MFI at 373 K during 100 minutes as a function of time.

Table 4. List of the Quantities that Are Calculated from the Time Based Experiments

quantity	description
intensity in range [6700,7350] cm^{-1} , I_1	Euclidean norm of the vector that corresponds to the spectrum in the [6700,7350] cm^{-1} range
intensity in range [8000,8700] cm^{-1} , I_2	Euclidean norm of the vector that corresponds to the spectrum in the [8000,8700] cm^{-1} range
total intensity, I_{tot}	Euclidean norm of the vector that corresponds to the spectrum when the absorbances are merged in one single vector

MatLab version 6.1 (MathWorks, Natick USA, version 6.1, 2001) was used to perform all calculations.

Results

The information of butane and isobutane is only located in a small part of the spectral range. Therefore, the performance of the spectroscopic method highly depends on wavenumber selection. After a preliminary study two spectral ranges are selected. The first range is from 6700 to 7350 cm^{-1} and also includes some water bands. The second range is between 8000 to 8700 cm^{-1} . These ranges correspond to CH_2 stretch + bend and CH_3 stretch vibrations, respectively. The intensity in the selected spectral regions appeared to be linearly dependent on gas pressure, although a small nonlinearity is still visible when y (spectral quantity) is plotted versus P (pressure). Different spectral preprocessing treatments were tried in this work and compared to no preprocessing (see Table 1).

Calibration Results. It is important to check whether the different treatments affect the performance of our calibration model. Using the raw data without preprocessing (option “None”) is not considered for calibration. For P_C the value of 60 kPa is selected. Figure 2 presents the calibration lines for (a) *n*-butane and (b) isobutane at 373 K using Drift correction, and the calibration lines for OffSet and Drift-WB are similar and therefore not presented. The solid lines are the linear regression models and the open symbols are the experimental results.

Table 2 (for the low pressures region, LP) and Table 3 (for the high pressures region, HP) present the residual standard deviation (RSD) of the calibration models with offset, drift and drift + water bands preprocessing techniques. These RSDs are in absorbance units.

The RSD value is directly related to the precision of the methods. Low values of RSD mean better prediction of P

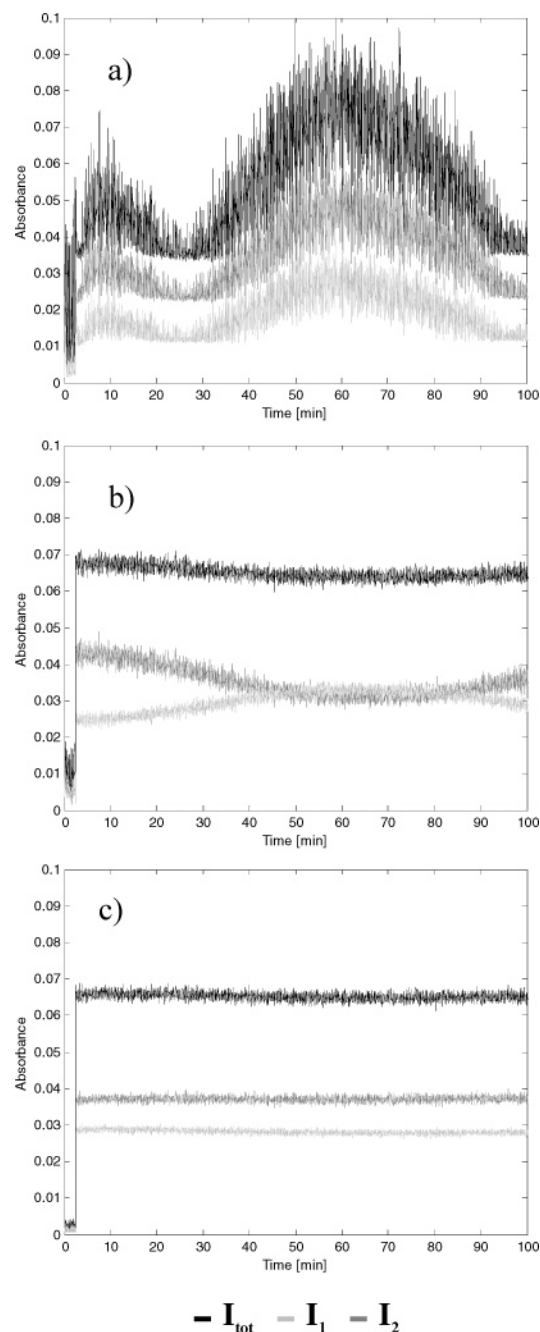


Figure 4. Norm of spectral ranges I_1 , I_2 , and I_{tot} as a function of time after preprocessing method: (a) None, (b) OffSet, and (c) Drift.

(pressure). From a close look into the tables, one can observe that all methods present RSD values with the same order of magnitude. Though a small improvement is observed when Drift-WB preprocessing is used.

Time Based Results. In the time based experiments, performed to measure the kinetics of adsorption/desorption, a spectral baseline drift was observed as a function of time. A representative example is presented in Figure 3. When the gas cell is empty ($P = 0$ kPa), the absorbance spectra do not show band like features; this is the initial step of desorption (0–2 min). When valve 2 is open, the pressure in the gas cell increases due to the *n*-butane desorption, giving the appearance of spectral bands (2–100 min).

To study the effect of the different preprocessing methods, three different quantities are derived from the each spectrum. They are listed in Table 4.

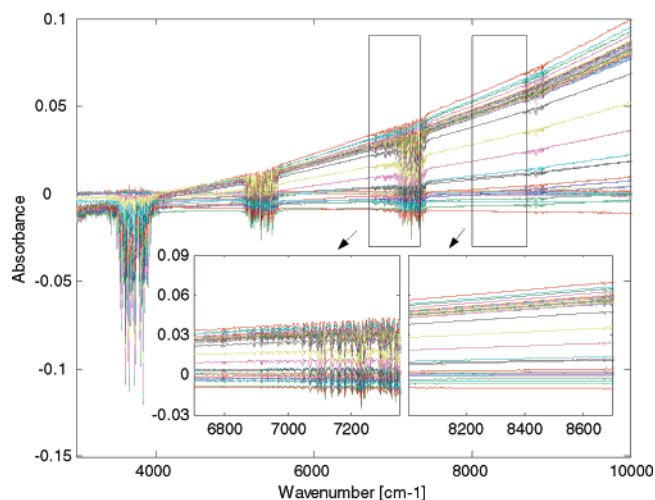


Figure 5. Blank raw spectra as a function of time. The two subplots have the same scale in ordinates.

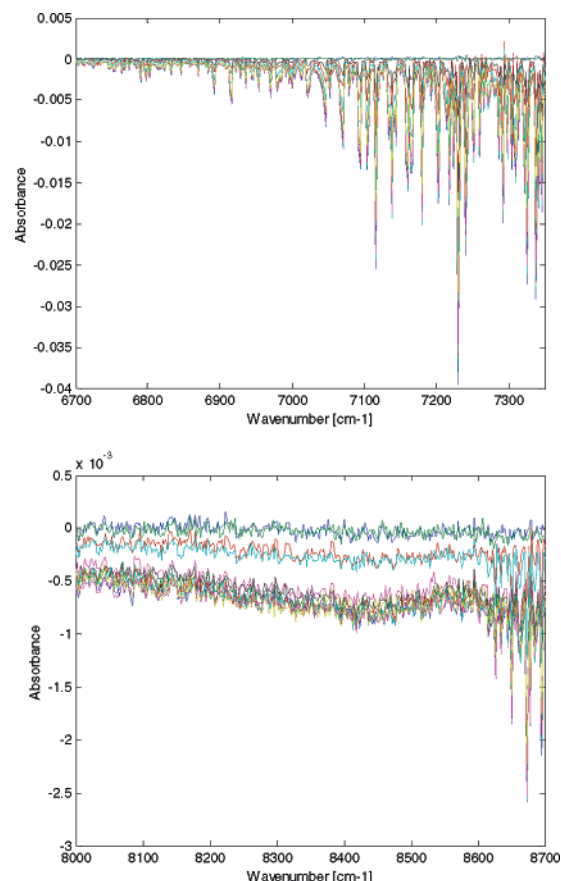


Figure 6. Drift corrected spectra for the 2 selected regions.

The ranges [6700,7350] and [8000,8700] cm^{-1} are indicated in Figure 3. During the initial step of desorption (0–2 min) these three intensities should be zero absorbance. When the desorption starts, the spectral quantities should sharply rise during the first few seconds, after which a plateau should be observed when the equilibrium pressure is reached. Spectral disturbance, such as drift, can mask desired analytical information about the adsorption process.

The time-based spectra were preprocessed by three methods: None, OffSet, and Drift. Figure 4 shows the norms of I_{tot} , I_1 , and I_2 as a function of time. Figure 4a shows that without preprocessing I_{tot} , I_1 , and I_2 curves

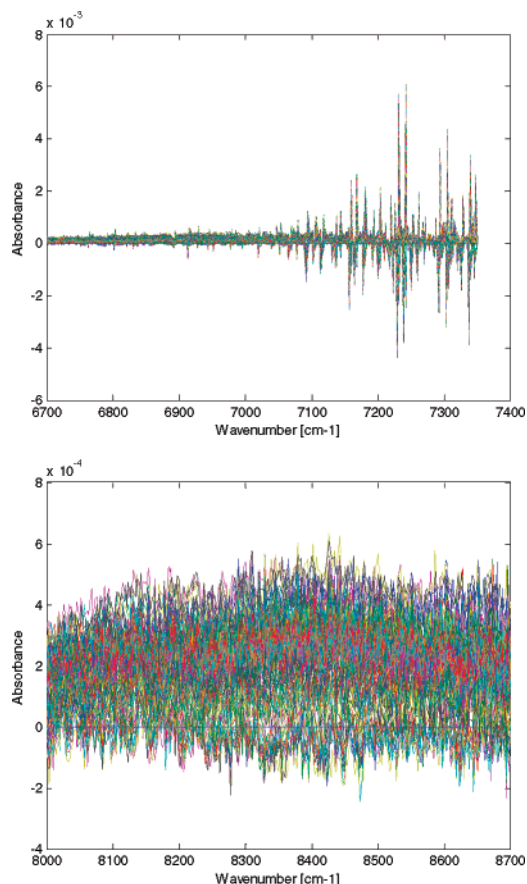


Figure 7. NAS spectra corrected for water band.

have high noise levels and do not present the expected plateau behavior. The instability masks the start of the desorption process completely. Second, OffSet preprocessing was performed (Figure 4b), and the norms of the resultant spectra were calculated and plotted in function of time. Though the I_{tot} curve behavior seem to represent a valid desorption experiment, one can observe that I_1 and I_2 curves are not plateau like, which indicates that offset treatment is not sufficient to correct the spectra. When two absorbance regions are used for analysis is not sufficient to evaluate the total intensity, I_{tot} . The “partial” quantities (I_1 and I_2) must present also the expected plateau behavior, since both regions are independent from each other. Figure 4c shows I_{tot} , I_1 , and I_2 curves for the drift preprocessing. These curves represent normal behavior, which indicates that drift correction eliminates all baseline problems.

Time-Based Control Experiment. Some checks were performed to find possible causes for this observed drift. Lamp intensity and voltage intensity were checked as a possible cause. A temperature effect in the detector and in the room humidity could cause such a problem. We recorded blank spectra and the temperature of the detector for 48 h in which the temperature would change from 18 to 23 °C. Blank spectra are spectra of the background conditions, and are representative also for a real experiment. The results are shown in Figure 5.

A clear baseline drift is observed in Figure 5. Water bands appear at 3900, 5700, 7200, and 8800 cm^{-1} . Both the baseline drift and water bands are time dependent. The blank spectra were treated in the same way as the spectra collected during a desorption experiments. Without treatment, the 1st region [6700, 7400] cm^{-1} contains intense water-bands, and in the 2nd region [8000, 8700]

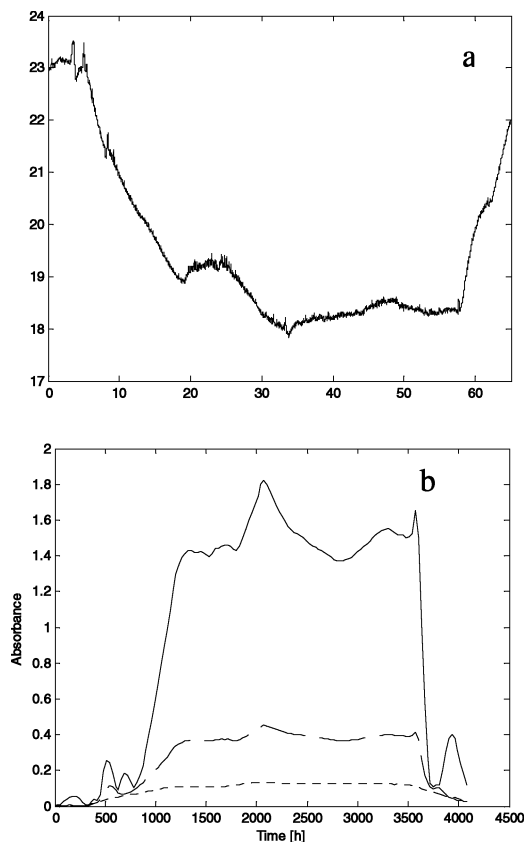


Figure 8. Temperature profile and I_{tot} in function of time for the 3 different preprocesses. (—) None, (---) OffSet, (- - -) Drift.

cm^{-1} , a baseline drift can be observed (subplots of Figure 5). OffSet correction reduces the baseline problem, but waterbands are still present. With Drift preprocessing the baseline is almost corrected; however, water-bands are still visible (Figure 6), mainly in the [6700, 7400] cm^{-1} region. The [8000, 8700] cm^{-1} region where the water bands were weaker is almost totally corrected by Drift preprocessing.

Figure 6 shows clearly that Drift is insufficient to correct for water bands, which disturb the data analysis. Therefore, also water-band correction is included in the preprocessing step. One of the final spectra of Figure 6 is selected, to represent the water band spectrum. All spectra are corrected for water bands using the NAS approach (see Figure 7). Although some spectral drift still remains, this is not significant, and the corrected spectra present mainly instrumental noise.

Figure 8 presents (a) the temperature profile and (b) intensity curves for the three treatments. The background spectrum was measured at 23 °C. The intensity is expected to be zero throughout the whole experiment. From the figure we can observe a clear deviation from zero intensity. One can also observe that pattern of the intensity curve is inversely related to the temperature profile. Drift results improved by a factor of 10 when compared with the results without any treatment (None), although the temperature effect (on the baseline drift or room humidity) is still visible after drift correction. The norm of the NAS vectors was calculated, and the resulting NAS signal was plotted as a function of time in Figure 9. In this case the NAS signal should have a similar magnitude as the other spectral norms used. A major improvement is observed after Drift-WB correction. The results of Figure 9 can be compared “directly” with ones presented in Figure 8b. Therefore,

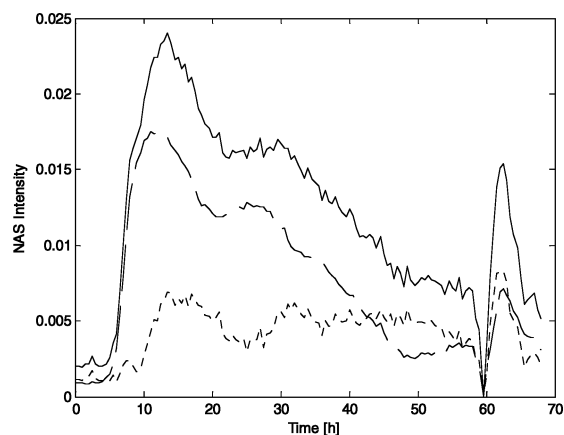


Figure 9. NAS vector norm (corrected for water-bands) in function of time. (—) Total, (---) Partial [8000, 8700] cm^{-1} , (- - -) Partial [6700, 7350] cm^{-1} .

one must pay attention that the scale of Figure 9 is 100 times smaller than the one in Figure 8b. The NAS signal is almost reduced to the noise level, which is in agreement with the fact that the data are from a control experiment, where only blank spectra were recorded.

The most robust method to preprocess time base data is drift correction, which can be improved when combined with correction of water bands. This treatment will be

adopted as the tool for data treatment on monitoring the adsorption/desorption time base experiments.

Conclusions

To access the adsorption kinetics we use a manometric setup coupled with a near-infra red (NIR) spectrometer. NIR spectroscopy presents the advantages of being a fast in-line analytical technique that allows us to quantify the isomers in the mixture, and it is nonintrusive. Spectral preprocessing is important, since a small change in temperature can produce drift problems and intensity change of water-bands in the spectra causing stability problems. Therefore, the Offset, Drift, and Drift-WB preprocessing techniques were studied to verify their effect in the performance of our calibration model and in the data analysis of the time based experiments. It was concluded that offset correction, drift correction and drift-wb correction performed equally well in the calibration case. Drift-WB technique corrects for these instabilities up to noise level in the case of time based experiments, whereas the other two techniques cannot eliminate the stability problems resulting from spectral drift and water bands. When online monitoring is required, data preprocessing cannot be only selected by the figures of merit of the calibration model but also by the robustness in time base analyses.

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