Fourier-Filtering Methods of Interference-Patterned Spectra in Multivariate Calibration and Prediction for Sample Identification and Thickness Determination

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Summary: Determining the thickness or identification of polymer materials with building a multivariate calibration model is based on the near infrared spectral information of the material. The spectrum of a thin plastic sheet is modulated by the interference of multiply reflected beams from the boundary surfaces and causes a disturbing signal component. On one hand, this yields unidentifiable samples or introduces large errors in the sample prediction set. On the other hand, interference-patterned spectra have to be excluded from the calibration set. Fourier-transformation of an interference-patterned spectrum vs. wave number leads to a Fourier-spectrum as a function of the optical path length (OPL) containing a well recognizable interference peak. After replacing these interference-components and performing an inverse Fourier-transformation, the spectra can be used for calibration or prediction. Two types of replacing were studied: the spline-interpolation on Fourier-spectrum vs. OPL and a novel method based on linear approximation between Fourier-spectra and thickness values. The effectiveness of each filtering method was tested on low-density polyethylene and polypropylene sheets.

Keywords: Fourier-filtering methods; infrared spectroscopy; interference-patterned spectrum; multivariate calibration; plastics

Introduction

In the recent years, near infrared (NIR) analysis has been steadily growing in popularity because of its ability to provide quick, non-destructive, qualitative and quantitative analytical information on a wide variety of materials from single pure, raw materials to complex products, like foods, textiles, cosmetics, medicals or polymers (see a wide array of applications described in the literature[1–4]). Light absorption in the NIR region (750–2500 nm) is primarily due to overtones and combinations of fundamental bands occurring in the middle infrared region. Lines are typically overlapped and very broad, leading to complex spectra. So univariate calibration methods are not suitable for this type of data. The use of suitable multivariate calibration (MvC) techniques, such as principal component analysis or partial least squares regression requires a relatively large number of calibration samples. The NIR technique with the potential of MvC methods suits excellently the identification or thickness determination of polymer materials.[5–9]

The spectrum of a thin plastic sheet is modulated by the interference of multiply reflected beams from the boundary surfaces and causes a disturbing signal component (cf. Figure 1). As also mentioned by Davies and Grant,[8] this interference pattern on the spectrum could make their analyses impossible and, on one hand, yields unidentifiable samples or introduces large errors in the

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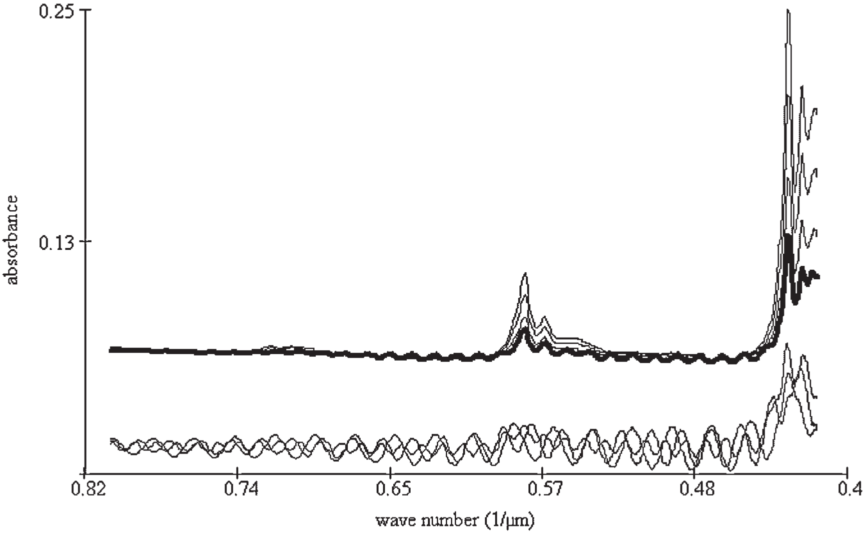

Figure 1.
Absorbance spectra of polypropylene (PP) and low density polyethylene (LDPE) polymer sheets (offsets for better viewing); — 14–38 μm PP (below), ▬ 25.5 μm LDPE, — 42–85.4 μm LDPE (above).

sample prediction set. On the other hand, interference-patterned spectra have to be excluded from the calibration set. In the thickness range where both interference-patterned (IP) and non-interference-patterned (NIP) sample spectra are available, it can be problematic to collect enough useable calibration spectra to build a robust MvC model and predict the thickness of samples with NIP spectra.

The goal of this work study is to overview the filtering methods,[10,11] that results in more accurate identification and thickness determination. Subjecting the IP prediction spectra to filtering fits to the MvC methods as a pre-processing step and allows the reuse of the interference-patterned spectra in the calibration process instead of their exclusion.

Theoretical Background

Considering a plane-parallel absorbing film situated between two non-absorbing media and normal incidence of light, the transmittance is the function of the wave number and thickness and is given by:[12]

$$T(k,h) = \frac{\frac{n_3}{n_1}\tau_{12}^2\tau_{23}^2 x}{1+\rho_{12}^2\rho_{23}^2x^2+2\rho_{12}\rho_{23}x\cos(\delta_{12}+\delta_{23}+\varphi)} \tag{1}$$

where $x(k,h)=\exp(-\alpha'(k)h)$, $\varphi(k,h)=4\pi\eta(k)hk$, $t_j(k)=\tau_j(k)e^{i\chi_j(k)}$ and $r_j(k)=\rho_j(k)e^{i\delta_j(k)}$ $(j=12,\ 23)$ are the complex transmission and reflection coefficients at the first and second interfaces. This formula is valid for both TE and TM waves if the factor n_3/n_1 is replaced by n_1/n_3 for a TM wave.

Transparent Region

Substituting $x=1$ and $\delta_{12}=\delta_{23}=0$ for Eq. 1 yields:

$$T(k,h) = \frac{\frac{n_3}{n_1}\tau_{12}^2\tau_{23}^2}{1+\rho_{12}^2\rho_{23}^2+2\rho_{12}\rho_{23}\cos(4\pi\eta hk)} \tag{2}$$

Then, the transmittance vs. the wave number k becomes a periodic function with

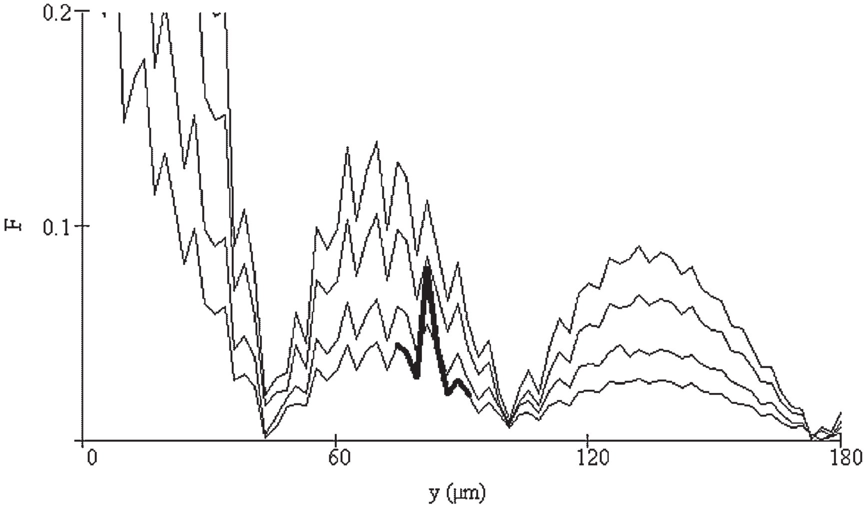

Figure 2.
Fourier-spectra of 25.5–85.4 μm LDPE sheets with ▬ interference peak.

a period of $1/(2\eta h)$. This finding is also valid for the absorbance.

Region of Strong Absorption

Multivariate calibration techniques rely on the presence of absorbance in the spectra, which contain the material information of the film. Using the approximation of $x \ll 1$ in the regions of strong absorption, Eq. 1 becomes much simpler:

$$T(k,h) = \frac{n_3}{n_1}\tau_{12}(k)^2\tau_{23}(k)^2\exp(-\alpha'(k)h) \tag{3}$$

Then, the absorbance of the plastic film (with negligible reflectance and scattering) is a linear function of the thickness (according to the Lambert-law):

$$A(k,h) = \log(T(k)) \approx \alpha(k)h - \beta(k) \tag{4}$$

Fourier-Transformed Spectra

Fourier-transformation of a transmittance or an absorbance (A) spectrum vs. wave number (k) leads to a Fourier-transformed spectrum (Fourier-spectrum) as a function of the OPL vertical to the sheet (y). The Fourier-spectrum (F) of an IP spectrum contains a well recognizable interference-peak (cf. Figure 2). Inhomogenities cause a peak-broadening, so a region near to the peak maximum has to be cut off and replaced. After performing an inverse Fourier-transformation, the spectra can be used for calibration or prediction.

Unfortunately, in the Fourier-range of the interference components, there are components related to spectral information of absorbance, on which MvC is based.

Replacing by Interpolation

Since the exact wave-number dependence of the complex refractive index of the sheet is not known, the exact Fourier-spectrum vs. OPL function is not known either. So replacing on the basis of the remaining part of the Fourier-spectrum can be done by interpolation on an own smoothed spectrum (see flow chart on Figure 3). With this method, replaced data become smooth and poor in details (see Figure 4), but can be used for identification and thickness determination too.

Replacing by Linear Regression

In case of thickness determination, another relation can be taken into account: a linear approximation between Fourier-transformed

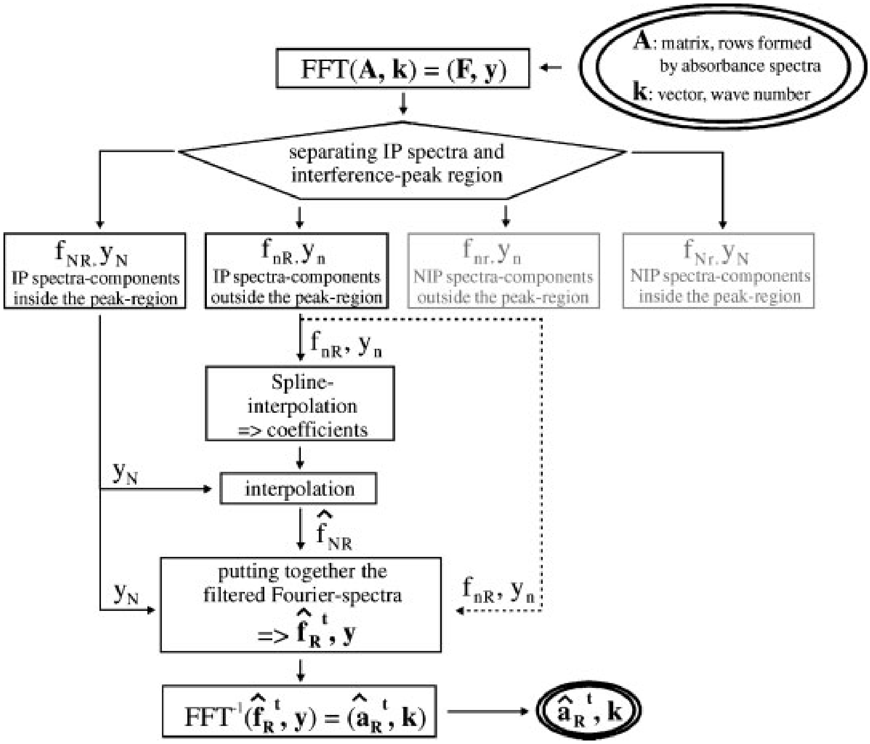

Figure 3.
Flow chart of replacing by interpolation.

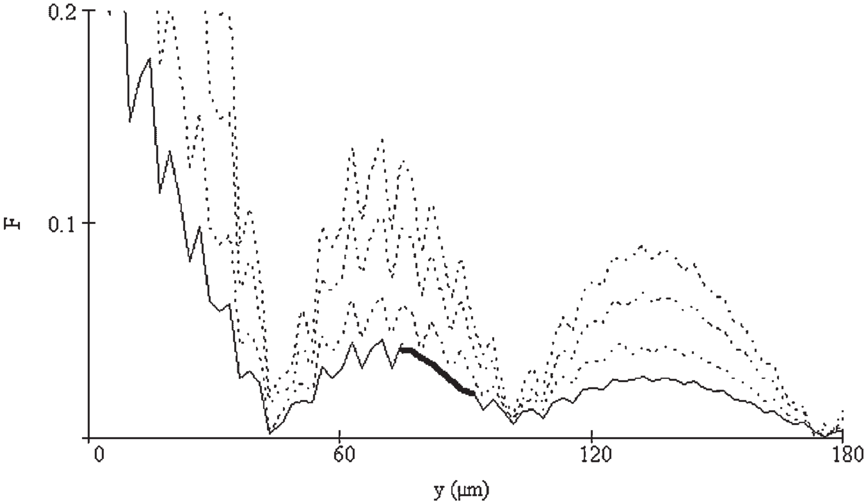

Figure 4.
Replacing by Spline-interpolation; — 25.5 µm LDPE with ▬ replaced components, - - - 42–85.4 µm LDPE.

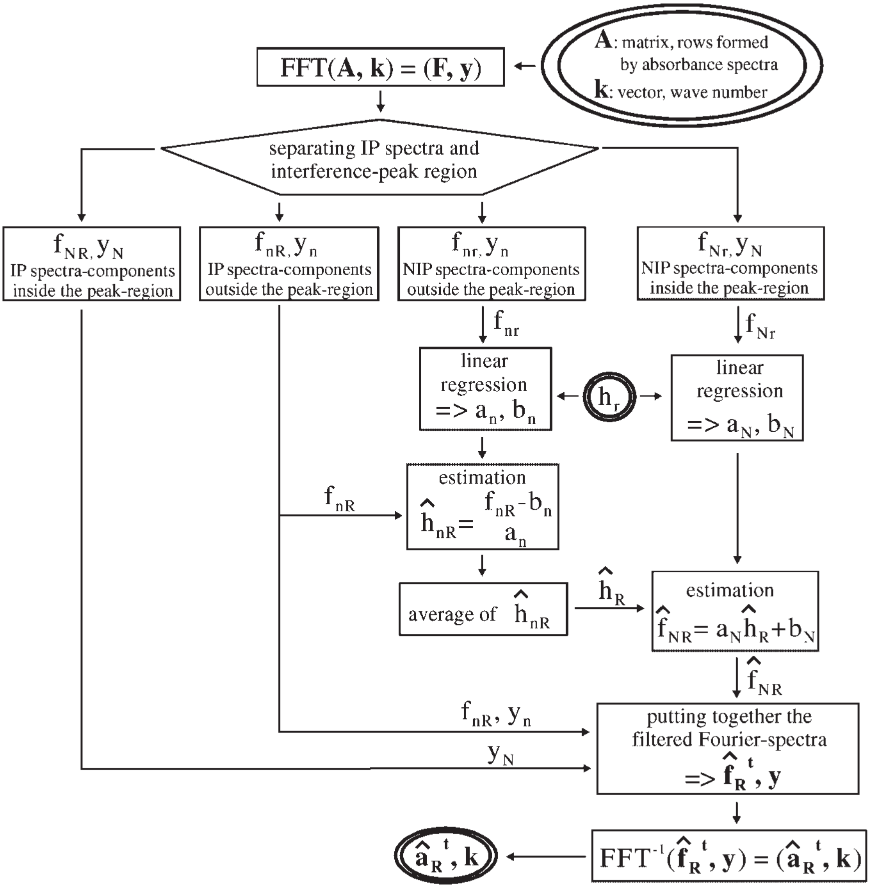

Figure 5.
Flow chart of replacing by linear regression.

absorbance spectra (from now Fourier-spectra, F), and thickness values (h). Its theoretical background is given by the Lambert-law (Eq. 4) and the linearity of the Fourier-transformation. With this method, all but the interference-patterned Fourier-spectra – which contain components at the deleted peak – and the corresponding thicknesses can be used for calculating regression coefficients and, finally, for replacing. If the IP-spectrum is in the prediction set, and its related thickness is not known, an estimation can be made. This means, that we calculate regression coefficients not only at the deleted, but at all other locations. Then we estimate thickness values at these locations and finally average them. Flow chart of this filtering method is shown on Figure 5.

This latter replacing method, compared to the previous one, yields more detailed filtered Fourier-spectra (see Figure 6).

In some cases, baseline corrections (for example a 2nd derivative process) have to be performed before the Fourier-transformation for reducing the strong disturbance of scattering.

Experimental Part

Materials

Low density polyethylene (LDPE) samples produced especially for us by Tisza Chemical Works (TVK, Hungary) were available with thicknesses ranging from about 20 to 80 μm. This means that some of the samples were thin enough to show IP spectra and

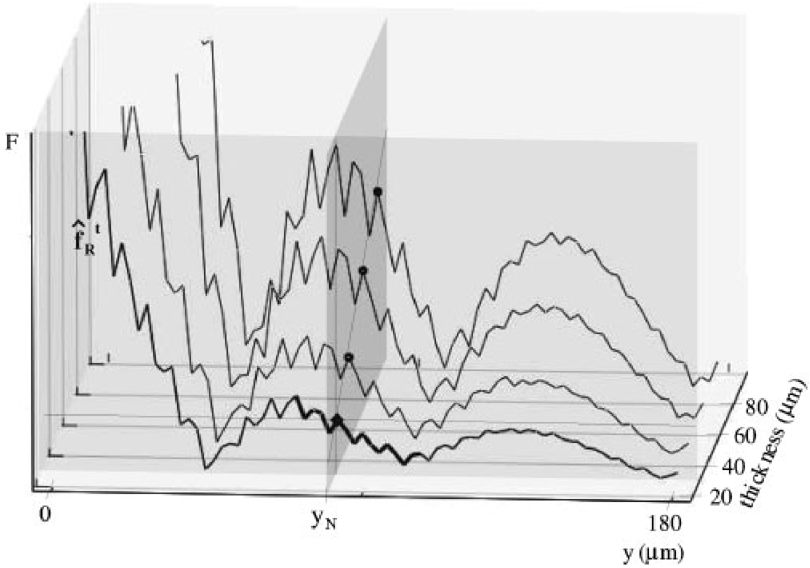

Figure 6.
Replacing by linear regression on Fourier-spectra vs. related thicknesses; ▬ 25.5 μm LDPE with ▬ replaced components, — 42–85.4 μm LDPE.

some of them were too thick or their quality was not as good as to show this pattern. Polypropylene (PP) samples from Radici Film Hungary under the trade name Biofol-KS were available with thickness ranging from about 15 to 40 μm all of them showing interference-patterned spectra. LDPE and PP samples were used for identification. The spectra of these two polymer materials contain absorbance peaks near to each other. LDPE samples were used for the thickness determination. Both types of samples were split into two sets, one for calibration (40 PP, 40 LDPE) and the other for validation (6 PP IP, 16 LDPE).

Thickness Determination

The thickness of the samples was measured at the same position used for spectral measurement by means of a digital micrometer (Mitutoyo) with accuracy of 1 μm. Thickness of the validation samples was measured 8 times, then averaged.

Spectrophotometer

Transmission spectra were collected by means of an acoustooptic tunable filter (AOTF) based spectrophotometer (type SINIS A, Siemens) equipped with an optical fibre. The spectral range of the measurement was 1200–2400 nm, with a sampling point at every 2 nm.

Software

The data were recorded and exported in txt format by using the application tool (APT) software of SINIS A. Additional calculations were performed in Mathcad,[13] and the MvC was made with GRAMS.[14]

Identification Method

We used PCA method[15,16] with cross validation (out: 1 files) and the data were mean centred and variance scaled. The analysis was performed on the second derivative of spectral data (gap: 16 points). Identification was provided by using the Mahalanobis-distance.[15,16]

Calibration Procedure for Thickness Determination

To build the calibration model, we used the PLS2 method[15,16] with cross validation (out: 1 file). The model was made with different parameters. Data were set or not mean-centered (MC) and variance-scaled (VS), regions of strong absorbance were selected or not, and the analysis was made on second derivative of spectral data with various gaps (4, 8, 16). To make predictions on the validation set, factors to be used were 1 or 2. The calibration model was chosen on the basis of the correlation coefficient between original vs. predicted thickness of the calibration set. The F-test ($\alpha = 0.01$) was applied to determine the statistical significance of outliers.

Filtering Parameters

The window-width parameter of the Fourier-filtering was 36 μm. The second derivative process have to be made before the filtering.

Calibration Model Performance: Comparison of SEPs

Calibration model performance was studied by taking the precision of the thickness determination on validation samples with standard error of prediction (SEP). Since both calibration models were validated on the same sample set, the calculated errors were correlated. Statistical tests were performed on a pair wise significance comparison of SEPs as recommended by Fearn.[17] Based on Fearn's criteria, comparisons of SEPs lead to SEP pairs with significant or non-significant differences.

Results and Discussion

We performed the above described calibration and validation procedure on different pre-processed spectra. Without Fourier-filtering, there is a possibility to make a calibration on all unfiltered spectra in the calibration set and, after that, a calibration on a restricted set from which part of the spectra (probably with interference pattern) could be excluded from the final calibration-model as outliers. In our case, no outliers were found but we built and tested a model in which spectra with interference pattern were excluded by Fourier-analysis. Influence of filtering in prediction set was tested by identification of the sheets and by thickness determination on thin (about 20 μm) samples showed very large amplitude interference-patterns.

We studied the influence of different filtering methods on the calibration model performance. So calibration models were built and tested on unfiltered or filtered spectra with components replaced by interpolation and on filtered spectra with components replaced by linear regression.

Table 1 shows results of these predictions.

In the case of filtered spectra, all of the PP and the LDPE foils could be easily identified. In case of the model on unfiltered PP spectra, separation was impossible, i.e., at least 5 out of the 6 foils were identified incorrectly. In case of the model

Table 1.
Prediction results.

Calibration model built on	Identification (correct/incorrect) for				Thickness determination (SEP values) for			
	Unfiltered PP	Filtered PP	Unfiltered LDPE	Filtered LDPE	Unfiltered predict. spectra thin LDPE	Filtered, replacem. by interp. thin LDPE	Filtered, replacem.by lin. regr. thin LDPE	All LDPE predict. spectra
Unfilt. cal. spect.								
all	1/5	6/0	13/0	13/0	11.8	3.22	0.68	1.26
NIP	1/5	4/2	13/0	13/0	10.74	–	–	1.4
Filtered, replacement by interp.	6/0	6/0	13/0	13/0	–	–	–	1.4
Filtered, replacement by lin. regr.	–	–	–	–	–	–	–	0.63

on unfiltered LDPE spectra, all samples could be identified correctly. The reason of this prediction difference is due to the smaller interference-modulation in the LDPE-spectra (in which case the longer wavelength end can be used).

The filtering by Spline-interpolation on thin prediction spectra results in a significant improvement in thickness determination. Thickness error of thin LDPE sheets is significantly the lowest after subjecting the prediction spectra to a Fourier-filtering based on linear regression.

After studying the influence of different filtering methods on the calibration model performance, the following can be concluded. In general, the calibration on filtered spectra with replacement by interpolation together with calibration on unfiltered spectra turned to perform the worst, whereas calibration on filtered spectra with replacement by regression gave significantly the best results. When unfiltered spectra are used in the calibration model, the calibration set becomes too small to build a well performing model after excluding the IP spectra and it is better to use the entire calibration set. It can be seen that filtering by Spline-interpolation is not a well suited filtering method in this case, but filtering by linear regression is.

Conclusion

Two types of Fourier-filtering were overviewed by testing their performances in identification and thickness determination of thin plastic sheets and in a calibration model. The spectrum of a thin plastic sheet is modulated by the interference of multiply reflected beams from the boundary surfaces and causes a disturbing signal component. This interference pattern on the spectrum could make the identification impossible and introduces large error in thickness determination. On the other hand, interference-patterned spectra have to be excluded from the calibration set. Nevertheless, it is a waste of information in the thickness region where just a few non-interference patterned sample spectra are available. Two types of replacing were studied: the spline-interpolation on Fourier-spectrum vs. OPL and a novel method based on linear approximation between Fourier-spectra and thickness values. The first method can be used for both identification and thickness determination. The latter method can only be used for thickness determination, but yields a more detailed filtered Fourier-spectrum.

It was shown, that the application of Fourier-filtering by Spline-interpolation allows a more precise identification of different sheets (PP and LPDE) as well as their thickness determination in comparison with those methods without filtering. Application of the Fourier-type filtering technique – replacing components of the interference peak using linear regression on non-filtered Fourier-spectra of the calibration set vs. the corresponding thickness values – led to significant improvements in thickness determination of plastic sheets and in calibration performance on the basis of significance comparisons of SEPs.

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