

Determination of residual paper content in plastic waste for recycling processes by near infrared diffuse reflectance spectroscopy

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Introduction

The recycling of consumer packaging becomes more and more important. In Germany the different fractions of household waste, for example, paper, glass, plastics, are collected separately. Each fraction is forwarded to a recycling process.

The plastics fraction represents 12.5% of all the recollected consumer waste packaging. In 1997 this was 69% of the total plastic sales packaging put on the German market.¹

To prepare the plastic household waste for recycling a multi-stage preparation process is necessary, including shredding, removing impurities and a compaction step. The result of this process is a granular semi-product of mixed plastics called agglomerate. These agglomerates are used in two different ways for plastics recycling. In feedstock recycling the plastics are converted into their starting materials, oil and gas. In mechanical recycling the agglomerates are converted into new plastic products. This is often carried out by extrusion. The re-extrusion process is considerably influenced by the residual paper content of the plastics recycling material. When the paper content exceeds 5 to 10% the extrusion mixture begins to char and the quality of the re-extruded plastics becomes insufficient.

Until now there is no reliable method for the quantitative determination of paper (cellulose) in a polymer matrix. This study describes an investigation into the use of near infrared (NIR) diffuse reflectance spectroscopy as a fast and cost-effective method for the quantification of the residual paper content in plastic waste.

Experimental

Preparation of the calibration samples and the agglomerate samples

Because there is no reference method for the quantitative determination of paper (cellulose) in a polymer matrix it was necessary to prepare a set of calibration samples with known paper content.

The calibration samples must contain a mixture of the most common plastics in post-consumer waste. Using data from other studies,²⁻³ the following composition of the basic plastics mixture was chosen: polyethylene (PE) 60%, polystyrene (PS) 20%, polypropylene (PP) 15% and polyvinylchloride (PVC) 4%. To this polymer matrix different quantities of a mixture of paper types used in the packaging industry was added to get a set of 12 calibration samples with paper contents from 0 to 11%.

For testing the calibration models we used seven different agglomerate samples. These agglomerates were real recycling samples collected by the company Deutsche Gesellschaft für Kunststoff-Re-

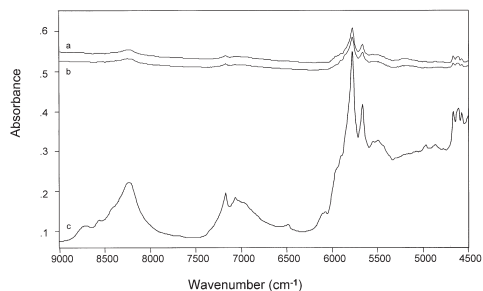


Figure 1. Diffuse reflectance spectra measured with the integrating sphere: (a) agglomerate sample, (b) calibration sample with 0.1% carbon black and (c) calibration sample without carbon black.

tion samples and the agglomerate samples are similar. This suggests that the polymer composition in both mixtures are nearly the same.

NIR measurements

The NIR diffuse reflectance spectra were measured with two different techniques, a hand-held diffuse reflectance probe and an integrating sphere. The diffuse reflectance probe FDR 320 (Axiom Analytical Inc., USA) was connected to an FT-NIR spectrometer, InfraProver II (Bran+Luebbe GmbH, Germany) by an optical fibre. The spectra were recorded with a spectral resolution of 25 cm^{-1} .

The integrating sphere was mounted as an external module to an IFS 66v spectrometer (Bruker GmbH, Germany). The samples were put in a rotating sample cup placed on this module. The spectra were recorded with a spectral resolution of 8 cm^{-1} . The spectral range for all spectra was $4,500$ to $10,000\text{ cm}^{-1}$.

Data analysis

The chemometric analysis of the spectral data was performed with three different software programs. The programs ICAP (Bran+Luebbe GmbH, Germany) and GRAMS32/PLSplus/IQ (Galactic Industries, Salem, NH, USA) were used for the quantitative analysis of the spectra from the hand held probe. The spectra measured with the integrating sphere were treated with the programs GRAMS32/PLSplus/IQ and OPUS/Quant2 (Bruker GmbH). In all cases the partial least squares (PLS) method was used.

The spectra used in the GRAMS and the OPUS programs were baseline corrected. The ICAP program does not have this function. All spectra were normalised on the most intensive

cycling mbH which is responsible for the plastics recycling in Germany. The agglomerates are grey and relatively inhomogeneous granulates. Their particle size is very different from the calibration samples. Therefore, both sample sets were finely ground to a homogeneous grain size distribution of $105\text{ }\mu\text{m}$ to $150\text{ }\mu\text{m}$.

The agglomerates as ground powder have a grey colour, whereas the basic polymer mixtures are white. This causes a baseline shift in the NIR diffuse reflectance spectra due to the different reflection properties of the samples [spectra (a) and (c) in Figure 1]. To match the reflection properties of calibration and agglomerate samples and to bring the baselines of the spectra closer together, 0.1% carbon black was added to the calibration samples [spectrum (b) in Figure 1].

Figure 1 shows that the spectra of the calibration

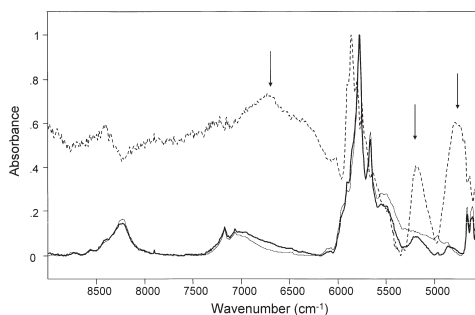


Figure 2. Diffuse reflectance spectra measured with the integrating sphere: — calibration sample with 0% paper, — agglomerate sample, - - - difference spectrum with marked cellulose bands.

band at 5780 cm^{-1} . For the calibration models the spectral ranges 4720–5330 cm^{-1} and 6200–7500 cm^{-1} were used.

Results and discussion

Figure 2 shows the NIR diffuse reflectance spectra of the calibration sample without paper and an agglomerate sample. The difference spectrum of these two spectra shows the three characteristic NIR bands of the cellulose spectrum, a broad band with a maximum at 6720 cm^{-1} representing the first overtone of the OH–stretching vibration and two OH–combination bands at 5190 cm^{-1} and 4750 cm^{-1} . Therefore, for the chemometric analysis the two ranges 4720–5330 cm^{-1} and 6200–7500 cm^{-1} were chosen.

Diffuse reflectance probe

The calibration results for the diffuse reflectance probe obtained with the two software programs ICAP and GRAMS32/PLSplus/IQ are summarised in Table 1. For the calculation of the calibration models four spectra of each calibration sample were used. The spectra of the sample with 5% paper were detected as outliers.

The two calibration models were tested with a set of spectra that were not included in the calibration. Spectra from calibration samples with the following paper concentrations were used for the test set: 1, 2, 3, 4, 6, 7, 8, 9 and 10%.

Figure 3 gives a comparison of the predicted paper content values and the true values. For the ICAP calibration model the maximum deviation from the true value is 1.7%. The standard error of prediction (*SEP*) is 0.9%. For the GRAMS calibration model the maximum deviation from the true value is 2.2%. The *SEP* is 1.3%.

Integrating sphere

Table 2 gives the results of the calibrations for the integrating sphere obtained with the two software programs Quant/OPUS and GRAMS32/PLSplus/IQ. For the calculation of the calibration models four spectra of each calibration sample were used. The spectra of the sample with 5% paper were detected as outliers.

The calibration models were tested with the same set of calibration samples as in the case of the diffuse reflectance probe. Figure 4 gives a comparison of the predicted paper content values and the true

Table 1. PLS regression results for the spectra measured with the hand held diffuse reflectance probe.

Software	Pretreatment	R^2	Factors	SE^a
ICAP	Normalisation	0.940	3	1.2%
GRAMS32/PLSplus/IQ	Baseline correction + normalisation	0.900	3	1.1%

^aSE - for ICAP standard error of estimation, for GRAMS standard error of cross-validation.

Table 2. PLS regression results for the spectra measured with the integrating sphere.

Software	Pretreatment	R^2	Factors	SE^a
OPUS/Quant	Baseline correction + normalisation	0.980	1	0.5 %
GRAMS32/PLSplus/IQ	Baseline correction + normalisation	0.974	1	0.8 %

^aSE - for OPUS standard error of estimation, for GRAMS standard error of cross-validation.

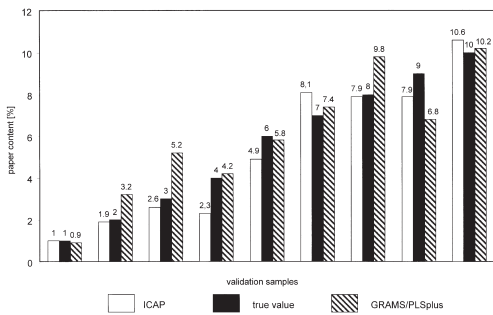


Figure 3. Test of calibration models—diffuse reflectance probe.

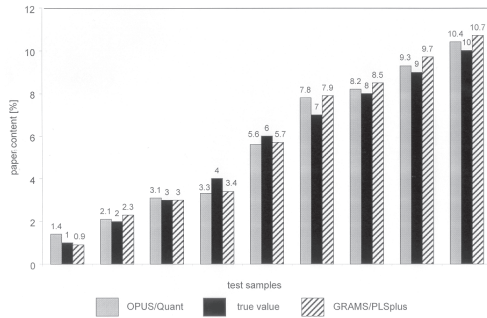


Figure 4. Test of calibration models—integrating sphere.

values. For the OPUS/Quant calibration model the maximum deviation from the true value is 0.8% and the SEP is 0.4%. For the GRAMS calibration model the maximum deviation from the true value is 0.9% and the SEP is 0.5%.

A comparison of the results given in Figures 3 and 4 show that the calibration models obtained with the spectra from the integrating sphere have a better prediction accuracy.

Prediction of the paper content in agglomerate samples

The NIR diffuse reflectance spectra of seven agglomerate samples prepared from different batches of plastic waste were measured with the hand-held diffuse reflectance probe and the integrating sphere. The four calibration models given above were used to predict the paper contents in the agglomerate samples. The prediction results for the different models are compared in Figure 5.

Since the true paper content values of the agglomerate samples are not known it is only possible to compare the relative variations in the prediction with the four different calibration models. One can see in Figure 5 that the two models calculated with the data from the integrating sphere give the most similar results. The maximum difference between the predicted paper contents is 0.4%.

The predicted values with the two calibration models obtained with the hand held diffuse reflectance probe are in the range of the values from the integrating sphere. But the variations of the results are much larger.

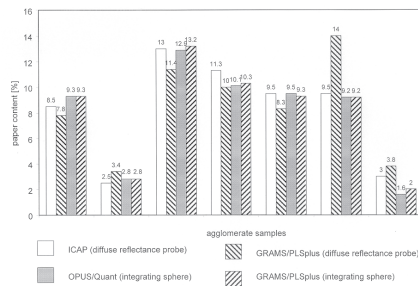


Figure 5. Prediction of paper content in different agglomerate samples.

Conclusions

Our study demonstrated that NIR diffuse reflectance spectroscopy is suitable for the quantitative determination of residual paper content in plastic waste.

A comparison of the results obtained with a hand-held probe and an integrating sphere with a rotating sample cup showed that measurements with an integrating sphere allow a more precise prediction.

To estimate the accuracy of the predicted paper content in the agglomerates a satisfactory independent reference method is needed.

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