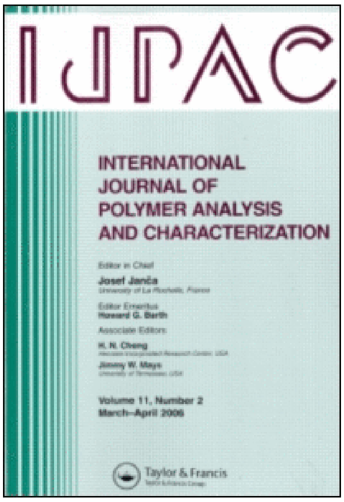

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Quantification of Antioxidants in Polyethylene by Near Infrared (NIR) Analysis and Partial Least Squares (PLS) Regression

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Partial least squares (PLS) regression was used to generate a calibration model that can be used for the prediction of the content of two antioxidants, Irganox 1010 and Irgafos 168, in high density polyethylene (HDPE). The samples containing levels of either one or both antioxidants in a range of 0–4500 ppm were analyzed by near infrared (NIR) in the diffuse reflectance mode. The samples were compounded in an extruder and subsequently analyzed as pellets; therefore, sample preparation was not required. High performance liquid chromatography (HPLC) was used as a reference method and the extraction of the antioxidants was performed either by microwave-assisted extraction (MAE) or ultrasonication. Data pretreatment of the raw NIR-data was necessary in order to eliminate the physical differences of the samples, e.g., size and shape. Multiple scattering correction (MSC) and second derivative of the raw data were used for this purpose. Root-mean-square error of prediction (RMSEP) for Irganox 1010 and Irgafos 168 was 46 and 97 ppm, respectively, when derived raw data was used; similar results were obtained when calibration was performed on MSC data. The number of principal components was determined by cross-validation; in addition, the calibration model was validated with a test set.

Keywords: Near infrared spectroscopy; PLS; Antioxidants; HDPE

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To effectively protect polyolefins during processing and exploitation, a stabilizer system is required. A combination of primary and a secondary antioxidant is often used due to their synergetic effect. Hindered phenols and phosphites are referred as to primary and secondary antioxidants, respectively. Phosphites act as hydroperoxide decomposers and hindered phenols act as radical traps. Because of the differing mechanisms, the effectiveness of using a combination of both types of antioxidants exceeds that of the individual components. During processing, phosphites are very effective in hindering degradation at processing temperatures and shear conditions. Hindered phenols impart good long-term thermal properties to polyolefins.

The amount and type of stabilizer determine the lifetime and performance of the polymer. Accurate measurements of additive contents are therefore very important. Traditional methods of additive analysis are generally time-consuming and tedious. These methods often require extraction with hazardous solvents and high performance liquid (LC) or gas chromatography (GC). Thermal analysis such as differential scanning calorimetry (DSC) can also be used for determination of antioxidant levels. This method provides no information about the concentration of different antioxidants separately but rather an overall assessment of the stability[1].

New methods for quantitative analysis of additives based on mid-infrared spectra and multivariate calibration have been presented[2,3]. One of the problems in the determination of additive levels by mid-IR spectroscopy is encountered during sample preparation. The samples are polymer films with small variations in thickness (due to errors in sample preparation). The differences in thickness cause a shift in spectra and methods for spectral normalization become necessary. These methods are reviewed and compared by Karrstang and Henriksen[3].

A technique that allows nondestructive analysis of polymers with very little or no sample preparation is near infrared (NIR) in the diffuse reflectance mode. NIR is based on measurements of light reflected by the sample when exposed to electromagnetic radiation in the range from 780 nm (12,820 cm^{-1}) to 2500 nm (4000 cm^{-1}). Qualitatively, this is the region between the visible red and the highest frequency used in conventional mid-infrared. Light in this range can be used to excite overtone and combination transitions of molecular vibrations and electronic transitions of highly conjugated systems. An overtone of a vibrational mode occurs when a single photon excites a molecular vibration from the ground state to a second or higher excited state. A transition from the ground state to the second excited state is called the first overtone transition, a transition from the ground state to the third excited state is known as second overtone transition, and so on. A combination band occurs when a single photon excites two or more different molecular vibrations. Only combinations and overtones involving higher frequency fundamentals are strong NIR absorbers, i.e., CH, OH, NH, C=O, COOH. Other vibrations have only higher order overtone bands in the NIR region, which are very weak as compared to the first and second overtones. For a given molecule, many active overtone and combination bands might be present in the NIR region giving, as a result, a spectrum with a large number of overlapping bands, which makes spectral interpretation difficult. The overtone and combination bands are approximately 10 to 100 times less intense than the fundamental bands of the mid-region; this allows (requires) the use of relatively large path lengths. For NIR transmission spectroscopy, thick samples (1 mm to several cm) can be used. For NIR diffuse reflectance, samples with large effective path lengths (granular samples with large particular sizes, or poorly scattering samples) can be directly analyzed without substantial preparation[4,5].

Different multivariate calibration techniques such as classical least square (CLS), multiple linear regression (MLR), principal component regression (PCR) and partial least squares (PLS) regression can be used to extract valuable chemical information from the spectral data[6]. PLS regression was used in this work to generate a calibration model for the prediction of the content of two antioxidants: Irgafos 168 and Irganox 1010 in high-density polyethylene (HDPE).

EXPERIMENTAL

Materials

High-density polyethylene (HDPE) powder containing no additives was supplied by Borealis AB (Sweden). Twenty-seven samples containing different levels of antioxidants were compounded in a Brabender twin-screw extruder at a screw speed of 70 rpm and a temperature of 210°C in the heating zones. The strands obtained in this way were subsequently pelletized. Pellets of approximately 3 mm diameter were subjected to NIR diffuse reflectance analysis. The concentration of both antioxidants varied from 0 to 4000 ppm.

Irgafos 168 (tris(2,4-di-*tert*-butylphenyl)phosphite) and Irganox 1010 (tetrakis[methylene 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]-methane) were supplied by Ciba Specialty Chemicals Sweden AB (Frölunda) and used as received.

Chloroform, hexane and acetone of analytical grades were purchased from Merck (Darmstad, Germany) and used as received.

Instruments

An FT-NIR Bomem MB series spectrophotometer with a DTGS detector and quartz-halogen source was used. The usable spectral range is from 14,000 to 3800 cm^{-1}. The samples were placed in a glass cup and scanned at a resolution of 4 cm^{-1}; 64 scans were averaged and each sample was scanned 15 times. The average of the 15 replicates was used for further multivariate data analysis.

An FTIR spectrometer Spectrum 2000 from Perkin Elmer equipped with a Golden Gate single-reflection accessory was used for attenuated total reflection (ATR) measurements on pellets. Each run was based on 20 scans with a resolution of 4 cm^{-1}.

Thermal analysis of the nonstabilized and some of the stabilized samples was performed on a Mettler Toledo differential scanning calorimeter with a DSC 820 module under a nitrogen atmosphere at a heating rate of 10°C/min. The values of the heat of fusion and the heat of fusion of 100% crystalline HDPE (293,1 J/g) were used to calculate the mass crystallinity of the samples.

A microwave extraction oven, model MES 1000 (CEM Corp., Indian Trail, North Carolina) was used to perform the extractions. The samples were extracted at 100°C during 30 min in a 50:50 (vol) mixture of *n*-hexane and acetone. Extractions were carried out at 70% of the oven's nominal power output. An ultrasonic bath Branson 2210 MTH (frequency of 45, power of 125), by Branson Ultrasonics (Soest, Netherlands) was also used for extractions.

A Hewlett-Packard high-performance liquid chromatograph HPLC 1090 provided with an UV diode-array detector was used for the quantification of the additives in the samples.

The SIMCA 5.2 software package from Umetrics Inc. was used for multivariate data processing.

Analytical Procedure

Pellets were analysed in a Bomen FT-NIR instrument between 4000 and 10,000 cm^{-1} with a resolution of 8 cm^{-1}; 15 replicates of each sample were obtained and averaged. Data pretreatment such as multiple scattering correction (MSC) and second derivative of the raw data was also used.

The levels of antioxidants in the pellets were controlled by HPLC preceded by either MAE or ultrasonic extraction; a detailed description of these methods is given elsewhere[7,8]. MSC and second derivatives were performed on the raw spectra. PCA was applied to discriminate polyethylene no-containing stabilizers from samples containing either Irganox 1010 or Irgafos 168, and PLS regression was carried out on 21 samples (calibration set) in order to make a calibration model, used to predict the content of stabilizers. A validation set with six samples was used to validate the model. The model was also tested by cross-validation.

The nonstabilized and some of the stabilized sample were analyzed by DSC and the approximate weight crystallinity was determined.

ATR-FTIR was performed on the nonstabilized and some of the stabilized samples in order to assess their oxidation level; attention was focused on the band at 1730 cm^{-1}, which characterizes the carbonyl region.

RESULTS AND DISCUSSION

The size and uniformity of analyzed particles are important when using diffuse reflectance methods since small particles tend to scatter the light, causing multiplicative shift in the spectra. Therefore the use of techniques that reduce the influence of such parameters in the measurements is necessary. The use of MSC as a method of normalization of the spectra is widely accepted. The second derivative of raw spectra is used for the separation of overlapped peaks and baseline corrections. This approach is a good way to obtain hidden information in the spectra, but one of the drawbacks is that the noise may increase.

Figure 1 shows the NIR spectra of the polyethylene powder before compounding Irganox 1010 and Irgafos 168. It can be observed that the identification and selection of specific bands or unique spectral features in the spectra is difficult. The variation in baselines is due to differences in scattering properties of the analytes. These variations can be eliminated by the methods explained above.

Figure 2 displays the spectra of the 21 calibration samples before (A) and after (B) MSC treatment. It shows that MSC is a useful technique for baseline corrections, as it eliminates baseline variations among different pellet samples.

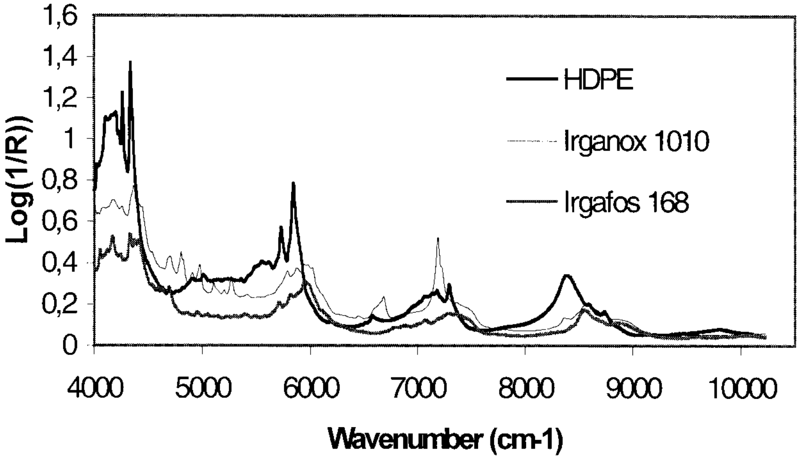


FIGURE 1 NIR spectra of Irgafos 168, Irganox 1010 and virgin HDPE.

Figure 3 shows the second derivative of the spectra in Figure 2A. Adequate separation of the spectral bands is achieved by this technique, which can be helpful for identification of the characteristic wavelengths of the analytes. A characteristic region for Irganox 1010 has been iden-

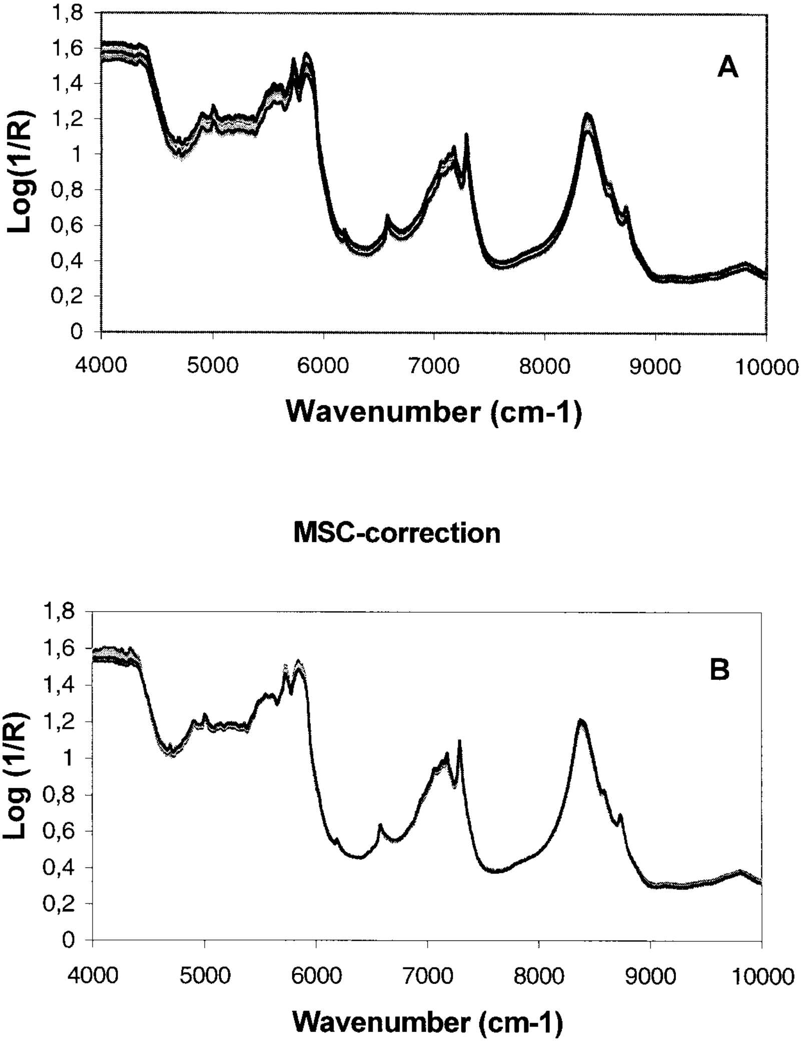


FIGURE 2 Raw NIR spectra of the 21 HDPE samples included in the calibration set (A) and multiple scattering correction (MSC) pretreated spectra (B).

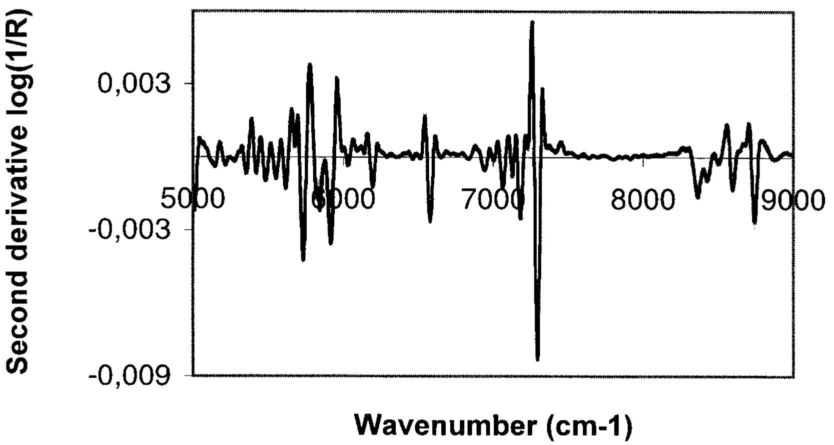


FIGURE 3 Second derivative of the spectra in Figure 2A.

tified between 6850 and 7350 cm^{-1}, which is a characteristic region for phenolic compounds[9]. This region has been used for calibration and quantification of Irganox 225 by others [10,11] with good results. However, the calibration in this work has been performed on the whole spectra in order to obtain the most information possible from the acquired data. A characteristic region for Irgafos 168 could also be identified between 4694 and 5230 cm^{-1}, which agrees with the P-O-Aryl region given in the literature[12].

Principal component analysis (PCA) was carried out on the NIR spectra; the score plots of the two first components are shown in figure 4. A certain relationship between the samples, which contain antioxidants, exists, since they are gathered in two clusters, whereas the virgin sample differs from the rest. The cluster on the left side is built by samples that contain a total amount of antioxidants lower than or equal to 2200 ppm, and the cluster on the right side is made up of samples having total antioxidant concentrations above 2500 ppm. The difference between virgin HDPE and stabilized samples may also be explained by the degradation of the virgin sample during extrusion, which has been confirmed by the presence of carbonyl groups and changes in crystallinity as measured by FTIR and DSC, respectively. The concentration of carbonyl groups was estimated by the carbonyl index (CI), defined as the ratio of the peak heights at 1730 cm^{-1} and the reference peak at 1464 cm^{-1}. The virgin sample showed a CI equal to 0.29, whereas the samples containing Irgafos 168 above 300 ppm did not show carbonyl groups at all. Samples with concentrations of Irgafos 168 below 300 ppm were slightly degraded; the CI was in the range 0–0.09. Small differences in the DSC crystallinity

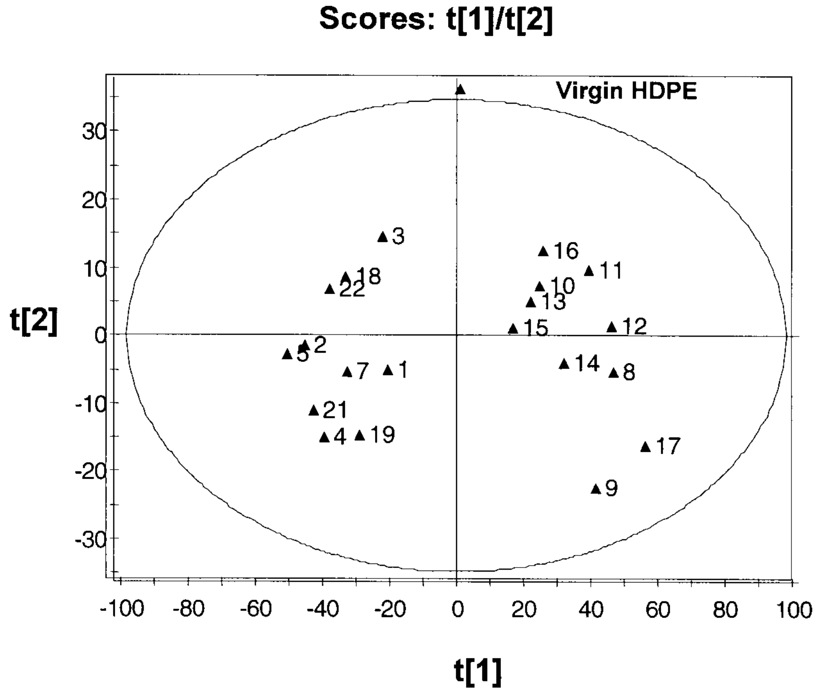


FIGURE 4 Score plot of PCA factor 1 and factor 2 for the calibration samples and the virgin HDPE based on the NIR spectra in the region 5000–9000 cm^{-1}.

were observed among the stabilized samples; their values were in the 62–65% interval. However, a lower crystallinity value, 57%, was obtained for the virgin specimen. The calibration models were generated based only on the stabilized samples.

The calibration curves for Irgafos 168 and Irganox 1010 based on the derived data are shown in Figure 5. The root-mean-square error of prediction (RMSEP) for Irganox 1010 and Irgafos 168 was 45 and 96 ppm, respectively. The models were obtained using a PLS regression with four factors over the 5000–9000 cm^{-1} spectral segment. The use of four factors can be explained because the bands of Irganox 1010 and especially Irgafos 168 are highly overlapped by the bands of polyethylene (Figure 1). The goodness (prediction ability) of the calibration models was proved by cross-validation and by predicting antioxidant contents of the samples in a test set.

Figure 6 shows the calibration curve for Irgafos 168 and Irganox 1010 based on the MSC pretreated data. The RMSPE for Irganox 1010 and Irgafos 168 are equal to 83 ppm and 96 ppm, respectively. Calibration

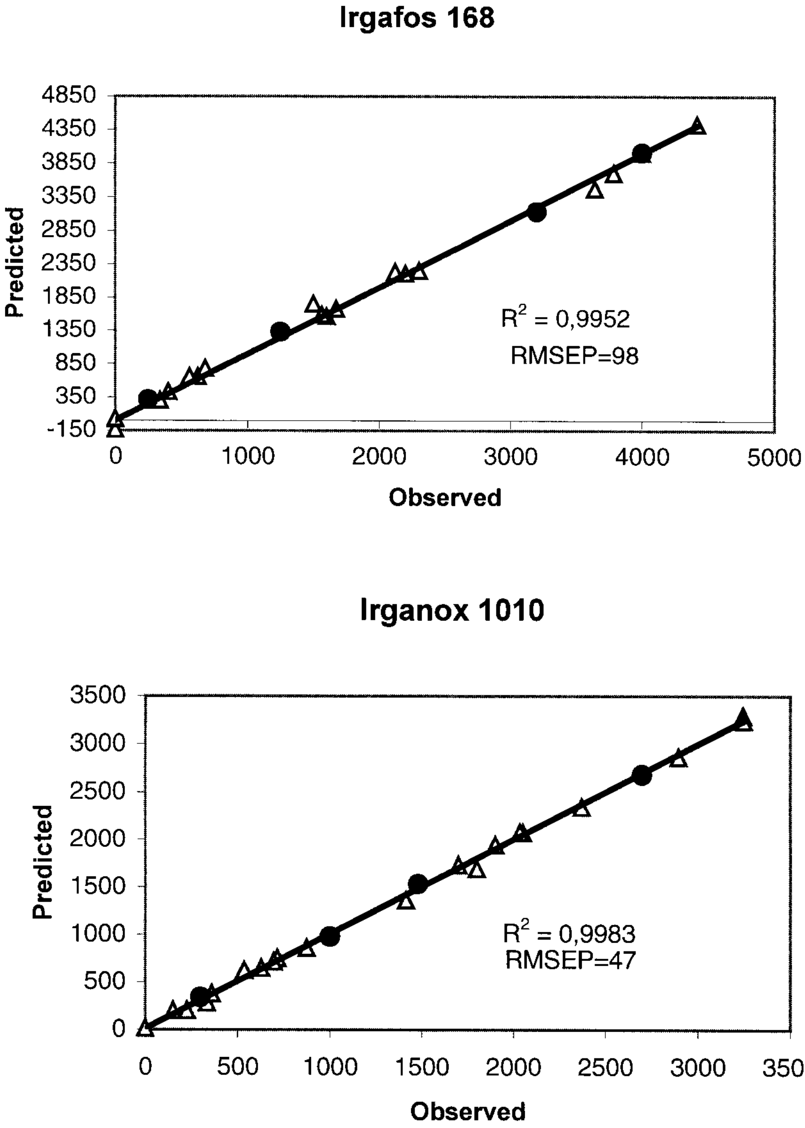
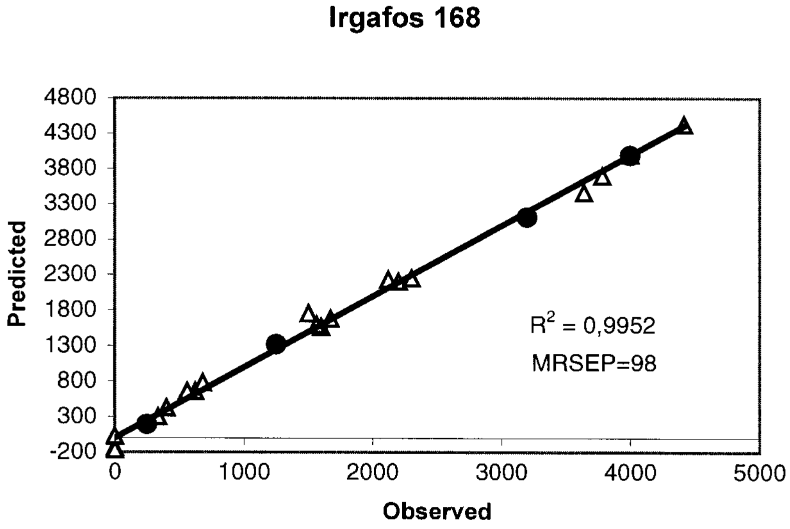


FIGURE 5 PLS regression calibration curves for prediction of Irgafos 168 (upper) and Irganox 1010 (lower) levels in HDPE from NIR spectra after second derivative treatment. Prediction set (Δ) and test set (●).



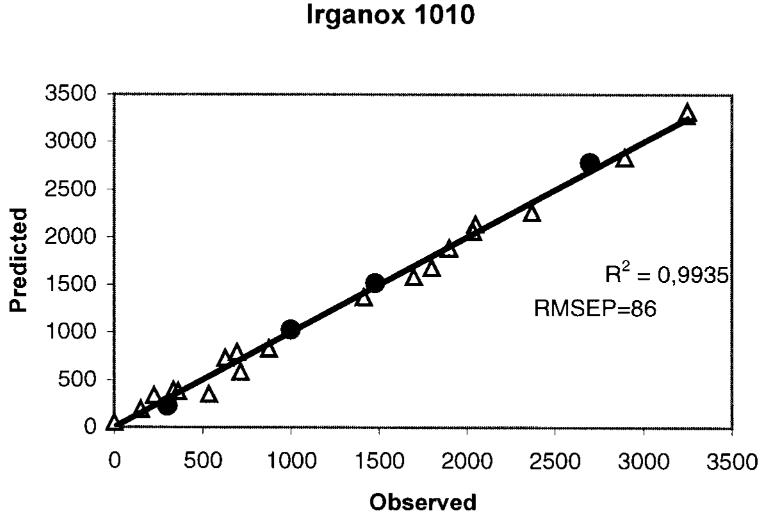


FIGURE 6 PLS regression calibration curves for prediction of Irgafos 168 (upper) and Irganox 1010 (lower) levels in HDPE from NIR spectra after MSC treatment. Prediction set (Δ) and test set (●).

was performed over the 4500–8000 cm^{-1} region, a region that contains unique spectral information about the antioxidants. However, even in this case, due to spectral interference between the HDPE and the antioxidants, four PLS factors were necessary to build the model. The models were validated as above.

CONCLUSIONS

NIR is a suitable method for quantification of antioxidants in polyethylene. The standard error of prediction is almost comparable to the error of wet methods, i.e., extraction plus liquid chromatography. The error of prediction of this method is 35 ppm for Irganox 1010 and 68 ppm for Irgafos 168. The inaccuracy in the quantification of Irgafos 168 is due to the fact that this antioxidant degrades during polymer processing. NIR is a fast method, which requires almost no sample preparation and can be easily used for at-line or on-line quality analysis (QA).

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