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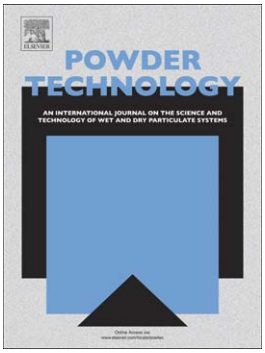

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Assessment of Near-Infrared (NIR) Spectroscopy for Segregation Measurement of Low Content Level Ingredients

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Abstract

Segregation in particulate systems may be caused by particle size, density and shape distributions leading to negative effects on product quality as well as the production costs. Quantifying powder segregation using a reliable and robust method is challenging, particularly for low content level ingredients. In this paper, we evaluate the application of NIR spectral analysis for detecting the extent of segregation of components in a multi-component mixture. As a model system, a typical laundry detergent formulation, comprising spray-dried powder, known as Blown Powder (BP), Tetraacetylethylenediamine (TAED) and enzyme placebo granules, is used. The effect of using different pre-processing methods on the measured component fractions is analysed. These are scatter correction using Standard Normal Variate (SNV) as well as derivative correction using first, second, Norris-Williams and Savitzky-Golay derivatives. The results from the NIR technique are compared to those obtained by image analysis. Concepts of Mean Absolute Error (MAE) and Mean Absolute Percentage Error (MAPE) are used to evaluate the accuracy of different pre-processing methods. The second derivative of Norris-Williams method shows the best pre-processing method for the quantification of low content level enzyme placebo granules in the ternary mixture of detergent powder. Using the proposed NIR technique and the optimum pre-processing method, the segregation index of a low content level ingredient, such as enzyme placebo granules, is estimated to be 0.71 for a ternary heap of washing powders.

Keywords: Powder segregation, Near-infrared spectroscopy, Laundry detergent powders, Pre-processing methods, Low content level ingredient.

Introduction

In many industrial sectors involved in manufacturing and handling of particulate solids, inhomogeneity in powder mixtures caused by segregation could have significant adverse impact on the product quality as well as costs of production. Segregation may occur during handling, transportation and storage in nearly all dry powder handling operations such as pharmaceutical, food, mining and agriculture. Segregation may occur due to differences in particles physical properties such as size, density and shape. Some operations aim to separate powders of different properties, such as in mineral processing. However, most processes aim to achieve a homogenous mixture [1]. In pharmaceutical industry, the variation of active pharmaceutical ingredients (API) content in tablets can cause batch failure. Inadequate amount of bleach in a box of laundry detergent or taste variations in a powdered drink mixtures caused by segregation phenomenon could raise customer dissatisfaction [2,3].

To quantify segregation, the first steps is to determine each component fraction in the powder mixtures in order to assess its content uniformity. The traditional methods are based on wet chemical analysis such as High Performance Liquid Chromatography (HPLC), which is very time-consuming. In addition some important solid-state information could be lost because the solid form is dissolved in a liquid to form a solution [4,5]. On the other hand, there are several powder-based methods for the assessment of component inhomogeneity, which are briefly reviewed below.

One of the reported methods of quantifying powder mixture uniformity is measuring the bulk particle properties, such as electrical or thermal conductivity. However, this method is not applicable for many materials. For example, only materials which are a good conductor of electricity can use conductivity characterisation to evaluate the homogeneity of components. On the other hand, high

effusivity is required for materials to evaluate the homogeneity of components using thermal methods [6-9].

Of the widely used non-invasive techniques for the determination of components fraction and powder mixture uniformity is the image analysis [10-14]. For this purpose, a captured image of a mixture is divided into several bins and then some statistical parameters such as standard deviation of the colour distribution of the bins are measured. The computed parameters are then used to calculate mixing indices. Image analysis technique offers an accurate means of analysing component uniformity in powder mixtures, but this technique cannot be used for the mixture of components with similar colours.

For material identification (independent of the particle colour), non-invasive spectroscopic techniques such as Near-Infrared (NIR) and Raman spectroscopy have been developed, which are based on the collection of spectral information at a number of spatial positions. These techniques have already found a wide range of applications in industrial processes to assess component homogeneity. They can be used either for offline or online analyses of samples [15-19]. The major advantage of Raman spectroscopy is that the spectra of minor components can be accurately distinguished for the analysis of component fraction. However, this method needs expensive capital investment as compared to the NIR technique. Furthermore, interference by florescence may make the detection of particles difficult. On the other hand, NIR spectroscopy is not affected by florescence and also offers fast and relatively cheap chemical imaging of components [20].

The NIR technique has been widely used in the literature for the prediction of component concentration in the mixture of powders, some of which are briefly reviewed below. Johanson [21] designed a successful in-line segregation measurement device using NIR spectroscopy in which the spectra of the pure components and the whole mixture in a sample could be used to estimate the fraction of components. Lin et al. [22] carried out an at-line NIR study to evaluate the concentration of four structurally similar active pharmaceutical ingredients (APIs) in seven samples withdrawn from powder blends to analyse the blend uniformity. NIR approach could successfully discriminate between the components despite their small amounts (less

than 0.96%). In-situ NIR chemical imaging technique was successfully used by Osorio et al. [23] to investigate in-line monitoring of the blending process of pharmaceutical powders and therefore to determine the mixing time. The system camera was placed below a blender to scan the blend in a non-contact manner. A 5-point fiber NIR optic system was implemented by Vanarase et al. [24] to monitor in-line API concentration at the discharge of a mixer to scan the whole continuous manufacturing line of pharmaceutical blending. This study demonstrated promising results on the application of the system for control of continuous manufacturing of drug products.

NIR spectroscopy gives information on reflected light from samples which consists of both chemical composition of samples as well as scattering effect arising from physical phenomena such as surface roughness, density fluctuation and variation in particle size. For component fraction data analysis, only the information on chemical composition of samples is required, while that associated with scatter effects needs to be eliminated. The scatter effects could be eliminated using spectral pre-processing methods, which are divided into two main categories of scatter correction and spectral derivatives methods. Scatter correction is mainly applied for adjusting the baseline shifts, whilst using derivatives both baseline shifts and non-linearities could be corrected [25]. Suitable pre-processing method for the spectral treatment of a material must be found for an accurate post-processing data analysis. The effect of different derivatives of Savitzky-Golay method was investigated by Chia et al. [26] to accurately predict the Soluble Solid Content (SSC) of pineapple. A good SSC assessment of pineapple was carried out using the second order Sovitzky-Golay derivative method. In another work, the importance of spectral pre-processing was demonstrated for age determination of blood stain [27]. Spectral pre-processing was carried out using scattering technique of Standard Normal Variate (SNV) for improving the accuracy of the results. In summary, spectral analysis of components using raw spectral data appears inadequate and pre-processing of spectra has widely been used.

In detergent industry, inhomogeneity of the formulated powder mixtures and in particular the minor components such as expensive enzyme granules could have significant economic as well as health and safety impacts. It is therefore desirable to improve the quality of the products by inhibiting the product inhomogeneity. In a recent study, Bittner et al. [28] implemented NIR and Raman spectroscopy for the evaluation of content uniformity of different washing powder brands. The Bruker Multi Purpose Analyzer (MPA) instrument and the PerkinElmer Raman Station 400 were used for NIR spectral analysis and Raman analysis, respectively. They reported a successful classification of all the washing powder samples using NIR spectroscopy. In contrast, Raman spectroscopy was suitable for the determination of only two ingredients as all spectra could not be recorded due to high fluorescence.

There is a lack of reported in-depth research on the evaluation of NIR technique for the content homogeneity of powders, particularly for accurate quantification of segregation of low content level ingredients. The objective of the present study is to investigate application of an economic and portable NIR spectroscopic probe (MicroNIR1700® probe, manufactured by JDSU Ltd) to estimate the component fraction distribution of powder mixtures. Laundry detergent powders are used as a model system to assess the content homogeneity. Different pre-processing methods based on scatter correction and derivatives are examined for the improvement of the accuracy of measurements, particularly for low content level ingredient such as enzyme granules. The classical least square method based on the analysis of mixture and pure component spectra is used for the optimisation of component fraction [21]. The validation of NIR method is carried out by the comparison of the results with those of image processing of the same powder mixtures for both binary and ternary mixtures. The proposed NIR technique with the optimum pre-processing method is then applied for the measurement of segregation index of low content level enzyme granules in a heap of ternary mixture.

2. Experimental

2.1. Material and sample preparation

The mixture of components comprise Tetraacetylethylenediamine granules (TAED, organic binders and water), spray-dried synthetic detergent powder (Arial LS Diamond), known as Blown Powder (sodium carbonate, carbonic acid disodium salt, benzenesulfonic acid, mono-C10-16-alkyl derivatives, sodium salts, carbonic acid sodium salt and silicic acid sodium salt) and enzyme placebo granules (primary alcohol ethoxylate, titanium dioxide, size distribution presented in Fig. 1 obtained by British standard sieve size analysis). BP and TAED are used as active cleaning agent and bleach activator in detergent formulations, respectively. Enzyme placebo granules are representing the actual enzymes applied for stain removal. High cost of enzymes as well as their low quantities (less than 2 wt %) in the final detergent formulations are the main driver for having their desirable distribution and uniformity. Therefore homogeneity assessment of this component is a crucial requirement in detergent industry. BP and TAED were obtained from Procter and Gamble (P&G), Newcastle Innovation Centre, while enzyme placebo granules were obtained from DuPont company, USA. Enzyme placebo granules were used to avoid exposure risk to enzymes.

Fig. 1. Particle size distribution of enzyme placebo granules, BP and TAED.

For validation of the results of NIR probe, thin layers of binary and ternary mixtures were prepared on a flat glass surfaces (Fig. 2). Enzyme placebo granules were added intentionally at specific areas in the ternary mixture. This enabled to accurately analyse the spatial distribution of the enzyme placebo component fraction in the ternary mixture using image processing.

Fig. 2. (a) Binary mixture of TAED and BP (b) ternary mixture of TAED, BP and enzyme placebo granules.

NIR spectra of individual components (both at the full size distribution as well as different sieve cuts) were recorded by a single scan of the sample on the flat glass surface (scan area equal to the detection area of the probe). However, for the mixtures a larger surface was prepared and a number of scans were made. For segregation

analysis of the low content level ingredient, a heap of ternary mixture was formed in a box shown in Fig. 3 (dimension of 0.2 *m*× 0.2 *m*× 0.015 *m*) and was divided into several segments for NIR analysis. A heap of powders could be generated by pouring the primarily mixed powders through a funnel into the box. The box used in this study has dividing blades enabling the extraction of samples from different regions within the whole mixture.

Fig. 3. The box used for making a heap of washing powder mixture.

2.2. Spectroscopic instrument and image analysis

The area of interest of mixture samples was divided into 28 different grids, each equal to the area of detection of the probe (Fig. 2). The reflectance spectra in each grid was obtained using the MicroNIR1700® probe. The probe was set up on an automated X-Y stepper (manufactured by SmartDrive Ltd) for an accurate scan of the mixture area (Fig. 4).

Fig. 4. The MicroNIR1700® set up.

The NIR set-up used in this study can enable analysing large quantities of samples and can significantly reduce the sample preparation time. Component fraction results calculated from the spectra of the probe were then compared with those obtained by the image processing of the same powder mixture for the validation of the NIR results. In this study, optical image processing was carried out using Photoshop 7 software (an effective image processing for the selection of pixel threshold [29,30]) as a benchmark for the evaluation of NIR. The picture of mixture was captured using a D3300 Nikon camera (24 mega pixel). Different stages for the measurement of component fraction of each grid using image processing are shown in Fig. S1, (Supporting Information). The results of components fraction of each grid in Fig. 2, obtained using image processing, are provided in Table S1, (Supporting Information).

2.3. Data analysis and spectral pre-treatment

The mixture spectral intensity was simulated by a linear combination of the spectral intensity of the pure components based on the local fraction (x_j) of each component following the approach of Johanson [21]:

$$F_{mix}(\lambda) = \sum_{j=1}^{n_{comp}} (x_j . FS_{pure}(\lambda)) \quad (1)$$

where $F_{mix}(\lambda)$, FS_{pure} (λ) and x_j are the average predicted intensity of the mixture, average intensity of pure components and area fraction of components, respectively.

The classical least squares method [21] was selected as the optimisation technique to minimise the sum of residual differences between the observed NIR intensity of the mixture, FS_{mix} (λ_k) and the average simulated intensity of the mixture ($F_{mix}(\lambda_k)$) according to Eq. (2):

$$Error = \sum_{k=1}^{n_{wave}} (FS_{mix}(\lambda_k) - F_{mix}(\lambda_k))^2 \quad (2)$$

where k is wavelength number. All programming and optimisation were done using Matlab R2014a software.

Spectral pre-treatment was done using SNV method as well as derivative algorithms as described below. SNV pre-processing technique (Eq. (3)) could be applied for removing scatter differences of samples causing different baseline changes between theoretically identical spectra [31].

$$FS_{i,SNV}(\lambda) = \left(\frac{FS_i(\lambda) - \overline{FS}_i(\lambda)}{S_i}\right) \quad (3)$$

where $\overline{FS_i}(\lambda)$, S_i and i are mean of each spectrum, standard deviation and grid number, respectively.

First and second derivatives are calculated numerically using the original reflectance spectral data according to the following equations:

$$FS_i'(\lambda_k) = \frac{FS_i(\lambda_{k+1}) - FS_i(\lambda_k)}{\lambda_{k+1} - \lambda_k} \quad (4)$$

$$FS_i''(\lambda_k) = \frac{FS_i(\lambda_{k+1}) - 2FS_i(\lambda_k) + FS_i(\lambda_{k-1})}{(\lambda_{k+1} - \lambda_k)^2} \quad (5)$$

First and second finite-difference derivative methods are very simple; however they may cause some detrimental effect on the signal-to-noise ratio [25]. Derivation techniques based on Norris-Williams and Savitzky-Golay are based on a smoothing method to reduce the signal-to-noise ratio within an acceptable limit [32,33]. In Norris-Williams pre-processing technique, the smoothing of original reflectance spectra can be obtained by Eq. (6):

$$FS_{smooth,i}(\lambda)_k = \frac{\sum_{l=-m}^{m} FS_i(\lambda)_{k+l}}{2m+1} \tag{6}$$

where m is the number of points around the measurement point of k. The first and second derivatives of the smoothed spectra can then be obtained.

In the Savitzky-Golay method, a polynomial curve is fit to a specific number of points of the original reflectance spectra. The first and second derivatives of the smoothed spectra can then be obtained and used in the optimisation. The polynomial order and the number of spectral points for fitting should be chosen based on the error minimisation [25]. The efficiency of the aforementioned pre-processing methods was evaluated by comparing the components fraction difference obtained from the NIR technique and the image processing. The value of mean absolute error (MAE) and Mean Absolute Percentage Error (MAPE) could show the efficiency of the pre-processing method for the estimation of components fraction according to the Eq. (7-9).

$$MAE_{overall} = \frac{1}{n_{grid}} \sum_{i=1}^{n_{grid}} \sum_{j=1}^{n_{comp}} \left| X_{Image\ analysis(i,j)} - X_{Method,(i,j)} \right| \tag{7}$$

$$MAPE = \frac{100}{n_{grid}} \sum_{i=1}^{n_{grid}} \left| \frac{X_{Image\ analysis(i)} - X_{Method,(i)}}{X_{Image\ analysis(i)}} \right| \tag{8}$$

$$MAE_{placebo} = \frac{1}{n_{grid}} \sum_{i=1}^{n_{grid}} \left| X_{Image\ analysis(i)} - X_{Method,(i)} \right| \tag{9}$$

where $X_{Image\ analysis,(i,j)}$ and $X_{Method,,(i,j)}$ are fraction data of component j using the image processing and NIR pre-processing method, respectively in grid i. n_{comp} is the number of components and n_{grid} is the number of grids.

Coefficient of variation concept (COV) was used as the segregation index for the samples extracted from powder heaps which can be calculated according to Eq. (10):

$$Segregation\ index = COV = \frac{\sigma}{\bar{x}_{Enzymeplacebo}} \tag{10}$$

where σ and $\bar{x}_{Enzymeplacebo}$ are standard deviation and the absolute mean value of enzyme placebo fraction of extracted samples, respectively.

3. Results and discussion

3.1. Effect of different pre-processing methods on the estimation of component fraction

Overall error analysis results using original reflectance spectra, SNV as well as the first and second derivative pre-processing methods based on $MAE_{overall}$ are listed in Table 1 for the binary and ternary mixtures as depicted in Fig. 2. For comparison, the minimum value of MAE error is highlighted in bold, which relates to the suitable pre-processing method for the estimation of components fraction. According to the $MAE_{overall}$ results in Table 1, the minimum value of overall error could be achieved using the second derivative method for both binary and ternary mixtures.

Table 1: Error analysis results using original reflectance, SNV, first and second derivative methods.

$MAE_{overall}$ results based on Norris-Williams derivation pre-processing method [32] for different m values (according to Eq. (6)) are presented in Table 2. It can be concluded that $MAE_{overall}$ results using the second derivative of Norris-Williams method have the minimum value for the binary mixture (m=4) and the ternary mixture (m=6).

Table 2: $MAE_{overall}$ results of Norris-Williams method.

$MAE_{overall}$ results of Savitzky-Golay pre-processing method [33] using different polynomial orders and different spectral points are presented in Table 3. The least $MAE_{overall}$ value is achieved by the second derivative and the polynomial order of 2 and 6 for binary (7 points) and ternary mixture (7 points), respectively. From the overall MAE error results so far, it can be concluded that the pre-processing method based on the second derivative of Savitzky-Golay is the optimum approach for the estimation of components fraction in both binary and ternary mixtures studied here.

Table 3: $MAE_{overall}$ results of Savitzky-Golay method.

In a number of studies, the combined derivative and scatter correction method is reported as the optimum method for pre-processing of spectra [34,35,36]. For example, Karande et al. [37] used SNV followed by the first derivative Savitzky–Golay method using nine points technique for eliminating NIR spectral scattering of blend components. In our work, the results of combined SNV with different derivative approaches for the estimation of component fractions of washing powders are shown in Table 4. It can be observed that the combined approaches could not reduce $MAE_{overall}$ of the component fraction results as compared to the derivatives method alone. According to the Tables 1 and 4, the SNV method is not suitable for the pre-processing of the spectra analysed here.

Table 4: Effect of SNV method followed by different derivatives on the component fraction of binary and ternary mixtures.

To see the effect of pre-processing approach on pure spectra of components as well as mixture spectra, they are depicted before and after applying derivative methods as shown in Fig. 5. For mixture, the spectra of grid 1 is considered as it contains the three components.

Fig. 5. Pure components and the mixture spectra obtained by NIR probe using: (a) original reflectance spectra (b) first derivative, (c) second derivative (d) second derivative of Norris-Williams method (m=6) and (e) second derivative of Savitzky-Golay method at P=6 and m=7.

MAPE results, as analysed by Eq. (8), of individual components using original raw reflectance, derivatives based on first and second derivatives as well as optimum points using Norris-Williams and Savitzky-Golay methods are reported in Table 5 for both binary and ternary mixtures. It should be noted that MAPE works well when there are no zero data. The error on zero data can be extremely high, making a false estimation using MAPE. For this reason, MAPE is not reported for low content level enzyme placebo granules as they produced zero data in the ternary mixture studied here. $MAE_{placebo}$ instead of MAPE is reported for enzyme placebo granules as shown in Table 5.

Table 5: Error results of individual components.

It should be noted that for the ternary system, the minimum overall $MAE_{overall}$ is obtained using the Savitzky-Golay method [33], (Table 3). However, $MAE_{placebo}$ and fraction results of the enzyme placebo (as presented in Table 5 and Fig. 6) show that the Norris-Williams method [32] based on the second derivative gives the smallest error for enzyme placebo granules. Thus, good care must be taken in choosing a good pre-processing method for the low level ingredient by taking account of the error result of the mixture as well as the individual components. According to the results of Table 5, the second derivative mode of Norris-Williams pre-processing method gives a good estimation of the enzyme fraction, the component being a low content level ingredient in a ternary mixture.

Fig. 6. Enzyme placebo fraction in ternary mixture obtained by image analysis, original reflectance and different pre-processing methods.

In fact, according to the nature of raw spectra data of each component, specific pre-processing methods could be beneficial for different spectra treatment [38]. Depending on the composition of powders and particle size distribution of each species, samples show different spectra patterns with baseline shifts and/or non-linearities [25]. Good care must be taken for applying the best pre-treatment method, as they could negatively affect the signal quality. Thus for each powder system, it is

important to select the appropriate pre-processing. According to the above-mentioned results, the pre-processing technique that uses derivative works better than the scatter correction method for the samples studied here. This treatment could be further improved by spectral smoothing. As previously mentioned, derivatives alone could have some detrimental effect on the signal-to-noise ratio. However, the most appropriate smoothing technique should also be investigated as some techniques could worsen the treatment. Savitzky-Golay method has broadly been used as a robust smoothing technique in many cases [26, 39-42]. However, it does not always offer the best spectra pre-treatment. For example, in the case of Kokalj et al. [43] it is shown that among different smoothing techniques, pre-processing using Savitzky-Golay method could not be appropriate for spectral treatment of biological samples as important information of spectra could be lost by this technique. In our case, the prediction of low content level ingredient of enzyme placebo granules is found to be more accurate using smoothing technique of Norris-Williams, as shown in Table 5. Some spectral information of enzyme placebo granules, which enables its differentiation from the spectra of BP and TAED during optimisation, could be eliminated using Savitzky-Golay method whilst preserved using Norris-Williams method.

Other researchers also suggested the use of specific methods for the spectral pre-processing of desired components. For example, Xu et al. [38] reported that the second order derivative was more suitable for the determination of protein content of wheat kernels amongst different pre-processing methods, while Moghimi et al. [44] suggested that scatter correction of SNV and first derivative provided the best results for the prediction of soluble solid content of kiwifruit.

The spectra variation analysis using the second derivative of Norris-Williams method (m=6) for a ternary mixture (of different enzyme placebo granules fractions) is shown in Fig. 7. The enzyme placebo granules are added to the mixture of BP and TAED as shown in Fig. 7 (a). In the first three samples, enzyme placebo granules are added to the bed of TAED particles, whilst in the next three samples, they are added to the bed of BP particles. It can be observed in Fig. 7 (b) that the spectra of mixture is gradually shifting to the spectra of pure enzyme placebo granules by increasing its

fraction. Comparison of the different pre-processing techniques shows that the Norris-Williams technique provides the lowest error for the prediction of the fraction of enzyme placebo granules for all samples shown in Fig. 7 (a) (error results are illustrated in Table S2). Therefore, variation between volume fractions of enzyme placebo granules does not change the optimum pre-processing technique.

Fig. 7. (a) Gradual addition of enzyme placebo granules on the bed of TAED and BP, (b) spectra viarition between different samples (obtained by second derivative of Norris-Williams method (m=6)).

From Fig. 6, it can be observed that the component fraction obtained using derivatives is more in agreement with those obtained by the image processing as compared to the raw original reflectance mode. Derivatives could correct the effect of baseline shifts and non-linearities arising from physical characteristic of particles such as size. In order to investigate the effect of particle size on the spectral analysis and the optimisation of components fraction, different sieve cuts of components have been analysed separately as follows. Particles were carefully sieved (ranging 250 μm to 1300 μm) using British standard size sieves and for pure component spectra, single sieve cuts were scanned (according to the method described in section 2.1) and analysed. The spectra curves of original reflectance, first derivative, second derivative as well as those obtained from Norris-Williams and Savitzky-Golay methods [32,33] for different sieve sizes (average size of the sieve cut) of enzyme placebo granules are presented in Figs. 8, 9 and 10, respectively.

Fig. 8. (a) Original reflectance, (b) first and (c) second derivative spectra of different sieve sizes of enzyme placebo granules (1290, 1009, 925, 780, 655 and 550 μm).

Fig. 9. (a) Norris-Williams spectra of original reflectance and (b) second derivative of Norris-Williams spectra (m=6) at different sieve sizes of enzyme placebo granules (1290, 1009, 925, 780, 655 and 550 μm).

Fig. 10. (a) Savitzky-Golay spectra of original reflectance and (b) second derivative of Savitzky-Golay spectra (P=6 and m=7) at different sieve sizes of enzyme placebo granules (1290, 1009, 925, 780, 655 and 550 μm).

It could be seen from reflectance curves that the spectra shift downward as the particle size is decreased, suggesting that different sizes in a mixture could influence the optimisation differently using original reflectance mode. The baseline shifts caused by the particle size of the component could be corrected by derivatives approaches of original reflectance spectra making the spectral to be more identical. However, a better treatment could be made by smoothing as they could reduce the detrimental effect of derivative pre-processing alone on the signal-to-noise ratio [32,33]. Similar analyses have been carried out for BP and TAED and the same conclusions are obtained (Fig. S2-S7, Supporting Information).

3.2. Case study: Evaluation of segregation of low content level enzyme granules after heap formation of ternary mixture using NIR technique

Segregation of components can be observed using heap formation of blended powder mixtures as particles of differing material properties can separate from each other during the pouring process [45,46]. As a case study, segregation of enzyme granules in a ternary mixture heap comprising BP, TAED and enzyme granules with 93/6/1 wt% is analysed. Heap formation and extraction of samples from the formed heap have been performed in the grid box shown in Fig. 3. Different stages which are required for the extraction of samples within the ternary mixture heap are shown in Fig. 11 (a). To estimate the average fraction of enzyme placebo granules in each extracted sample, thin layers of them were spread on a glass slide and scanned by NIR probe and image processing method, according to the procedure described in section 2.1. The optimum pre-processing method for enzyme placebo granules (reported in section 3.1) has been used for the measurement of enzyme fraction using NIR technique. Image processing of the enzyme placebo granules was achieved after capturing their picture exposed to a Light-Emitting Diode (LED). During LED light

exposure, the white colour of enzyme placebo granules was changed to dark purple due to fluorescence effect, nevertheless detectable by image analysis ((Fig. S8, Supporting Information). Enzyme placebo fractions measured for a number of extracted powder mixtures (highlighted in red in Fig. 11 (b)) using the proposed NIR technique are shown in Fig. 12 and compared with the image analysis results. A relatively good agreement between the results of NIR technique and image processing is observed.

Fig. 11. (a) Different stages of sample extraction in ternary heap (b) grid marked heap.

Fig. 12. Enzyme placebo fraction for the ternary heap of laundry detergent powders obtained by the proposed NIR technique and image processing.

The segregation index of the enzyme granules could then be measured using Eq. (10). Segregation index of enzyme granules obtained from NIR analysis (calculated for completely filled cells highlighted in red in Fig. 11 (b)) is found to be 0.71 which is close to that obtained using image processing (0.64). Calculation steps of the segregation index using both techniques have been summarised in Table S3, (Supporting Information). The percentage difference of the proposed NIR method relative to image analysis for the quantification of segregation of low content level enzyme placebo is estimated to be 10 %. Relatively high segregation index estimated for enzyme placebo granules in the ternary mixture studied here could be as a result of density variations between components. The bulk tapped density of the mode size of enzyme placebo granules is measured as 1450 $kg.m^{-3}$ which is higher than 489 and 414 measured for TAED and BP, respectively. Dense enzyme placebo granules could behave as if they are small and could build up more into the centre of heaps by a mechanism known as push-away effect. This could be one reason for having less enzyme granules in grid 2, 7 and 8 (towards the surface of the heap) than grid 10, 11, 13 and 14 in the centre of the heap (Fig. 12). The results of case study show that full analysis of the heap of powders for segregation estimation of low content level ingredients could be performed using the proposed set-up.

Conclusions

NIR spectroscopy was applied to the analysis of homogeneity of binary and ternary mixtures. As a case study test material, a typical formulation of laundry detergent powders comprising BP, TAED and enzyme placebo granules was used. NIR spectroscopy using MicroNIR1700® probe and the concept of classical least square method based on the analysis of mixture and pure component spectra was used for the quantification of components fraction. Raw reflectance data as well as data obtained by different pre-processing methods were used for the spectral analysis. It is found that spectral pre-processing using derivatives can be used to correct the baseline shift and non-linearities arising from differing physical properties of the components such as particle size. The second derivative of Norris-Williams pre-processing method shows the best optimisation technique for the quantification of low content level enzyme placebo granules in the ternary mixture of detergent powder. The results have demonstrated that powder segregation analysis of low content level ingredients can be successfully achieved using the proposed NIR technique. The approach enables the whole content of segments taken from the heap to be analysed. The percentage difference of the proposed NIR method for the quantification of segregation of low content level enzyme placebo in a heap of ternary mixture is around 10 %.

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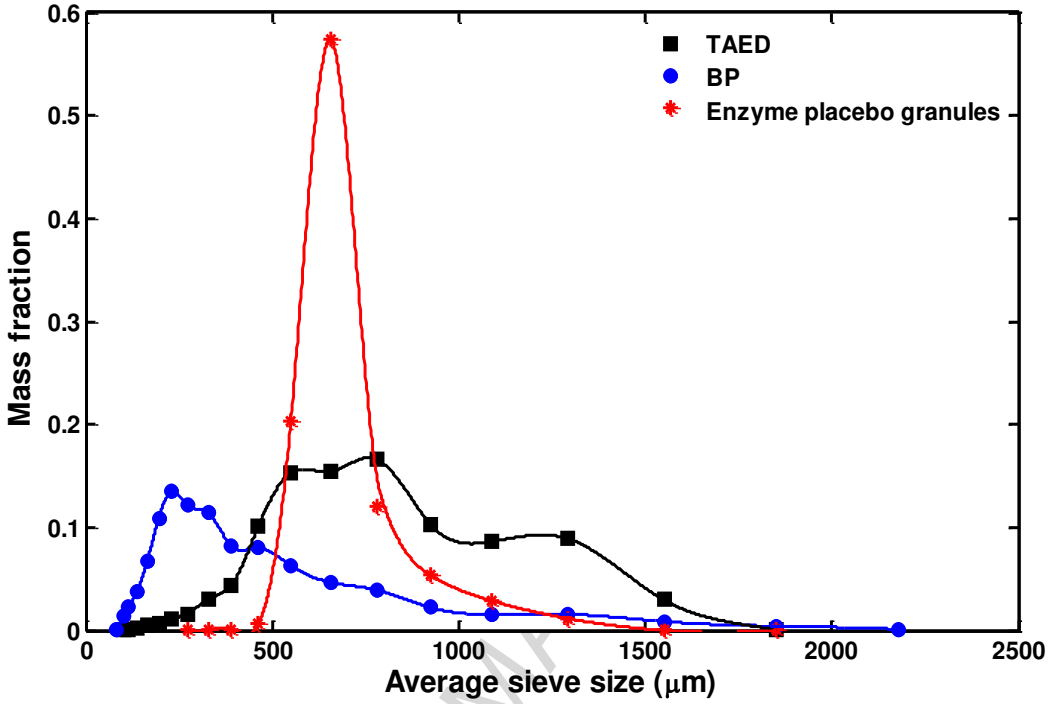


Fig. 1. Particle size distribution of enzyme placebo granules, BP and TAED.

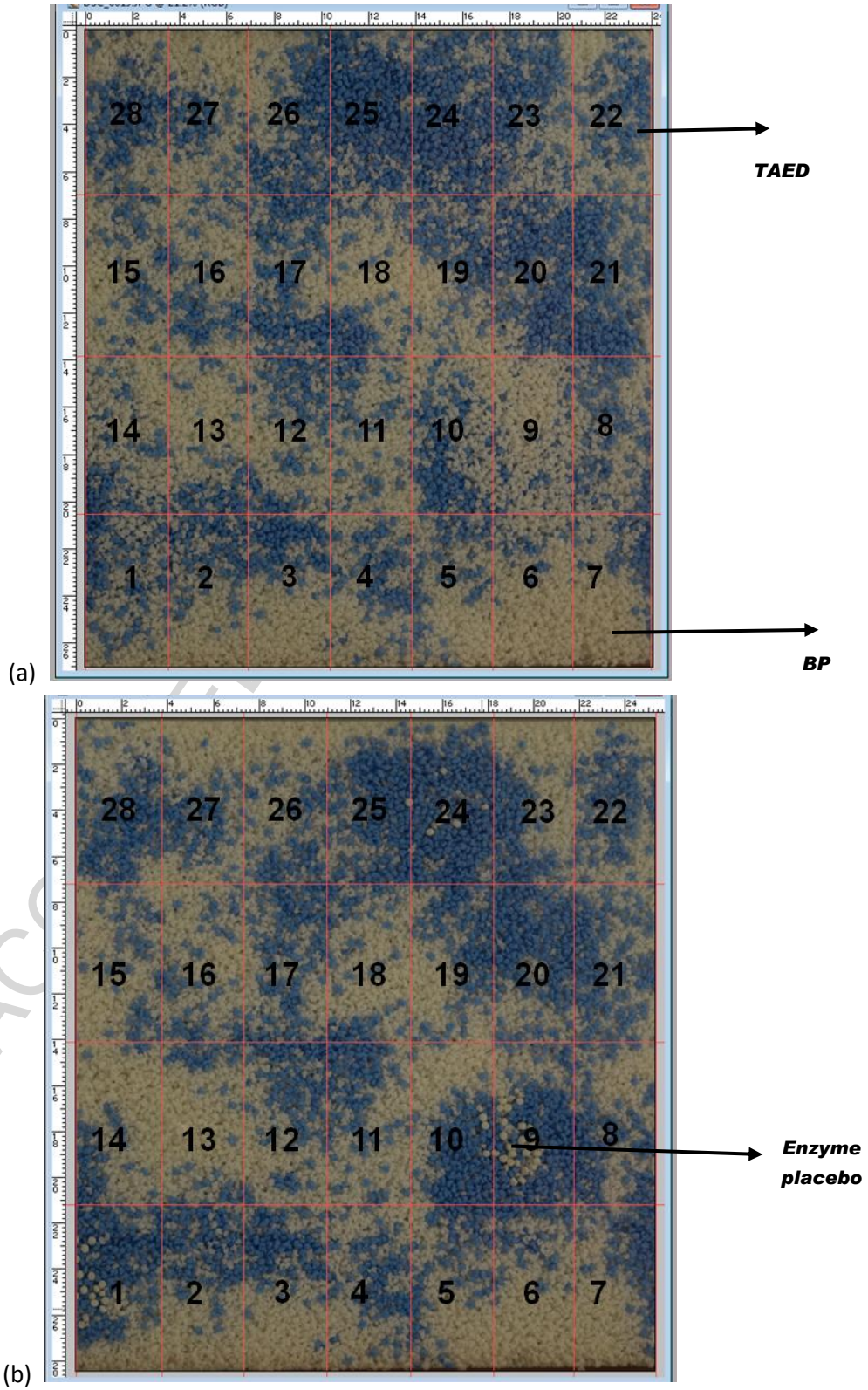


Fig. 2. (a) Binary mixture of TAED and BP (b) ternary mixture of TAED, BP and enzyme placebo granules.

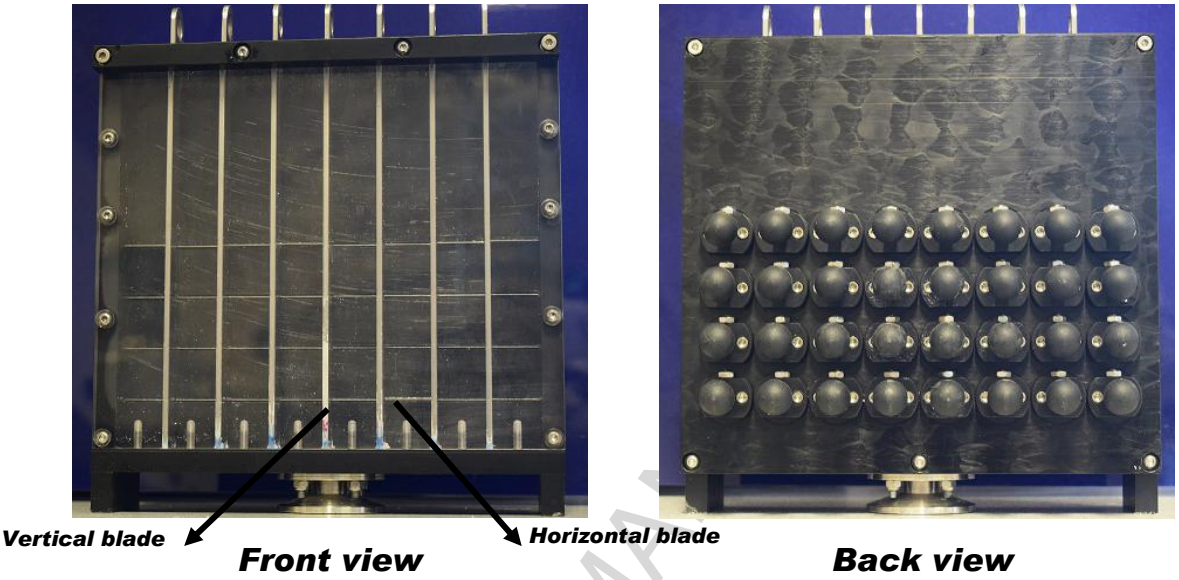


Fig. 3. The box used for making a heap of washing powder mixture.

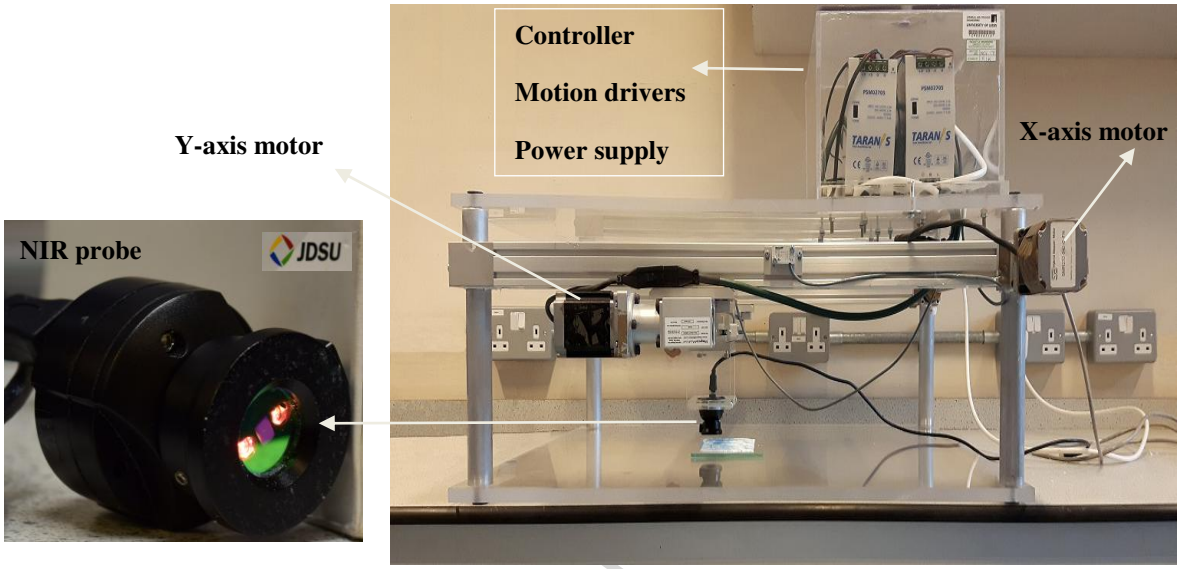
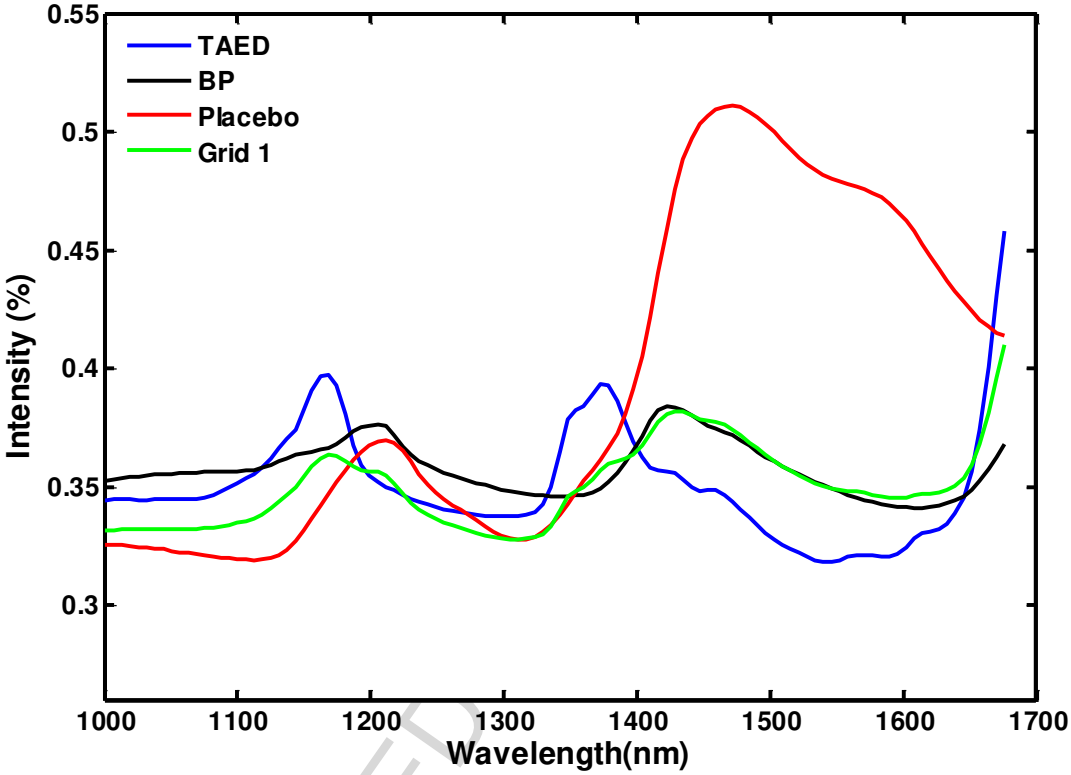


Fig. 4. The MicroNIR1700® set up.



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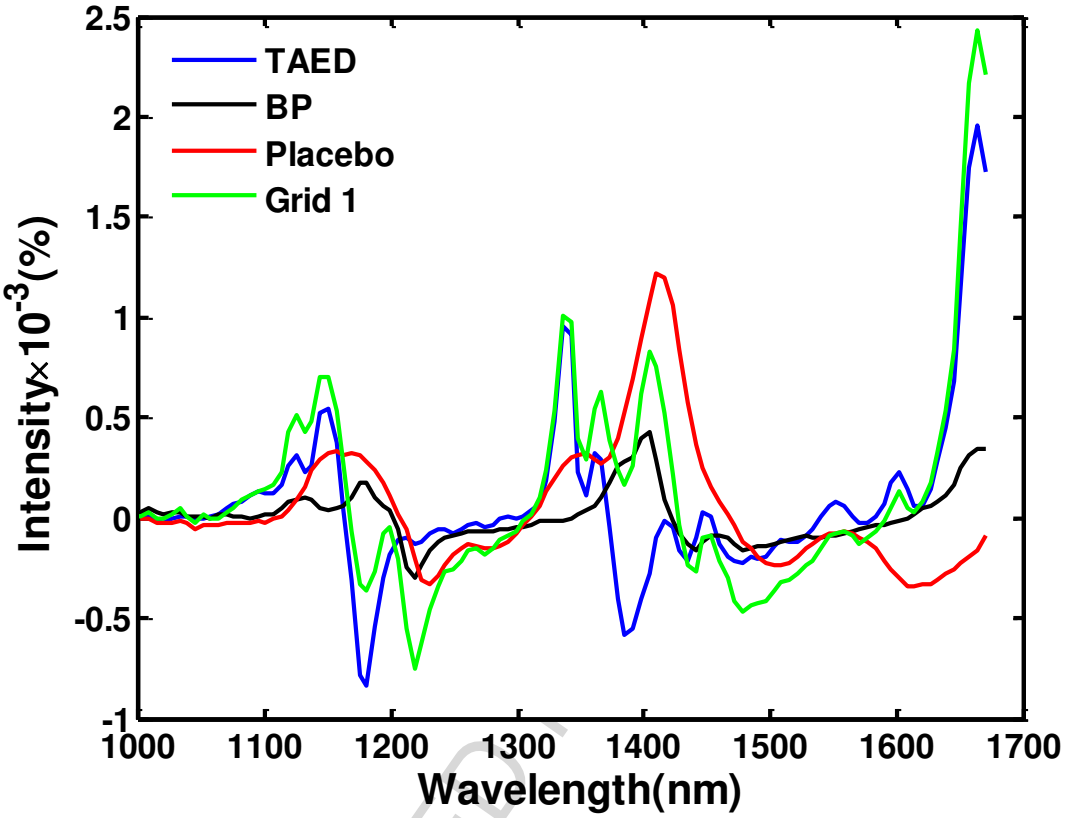

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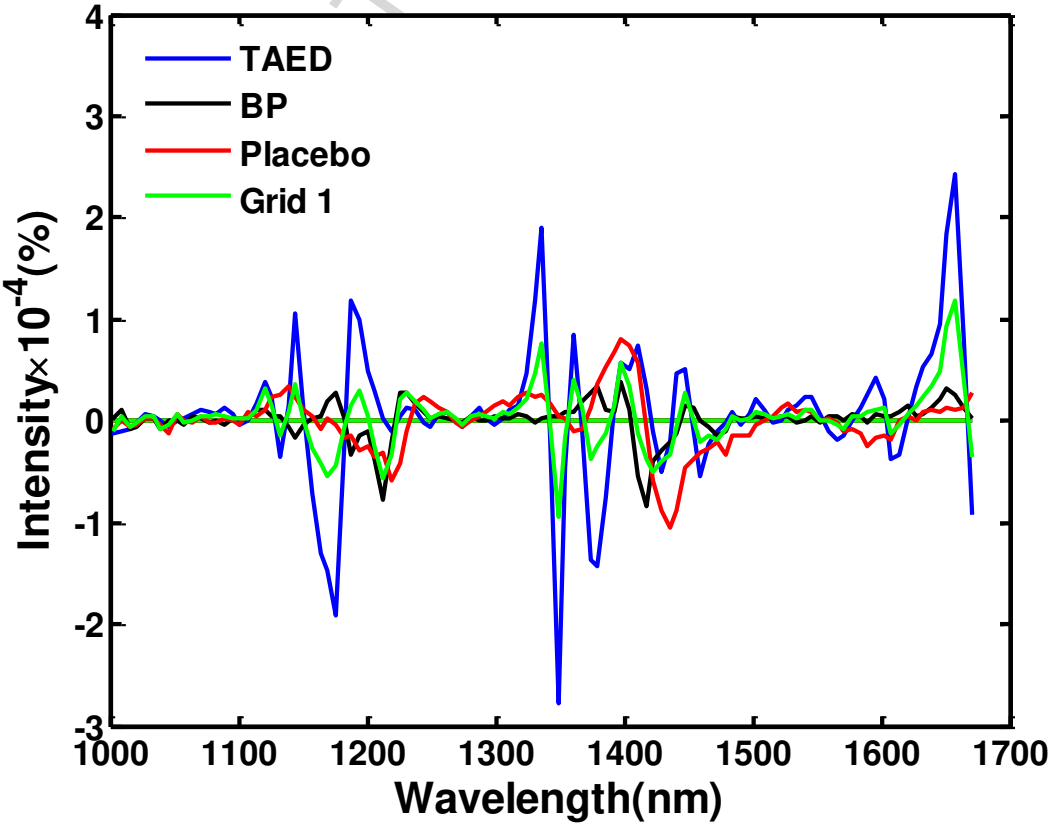

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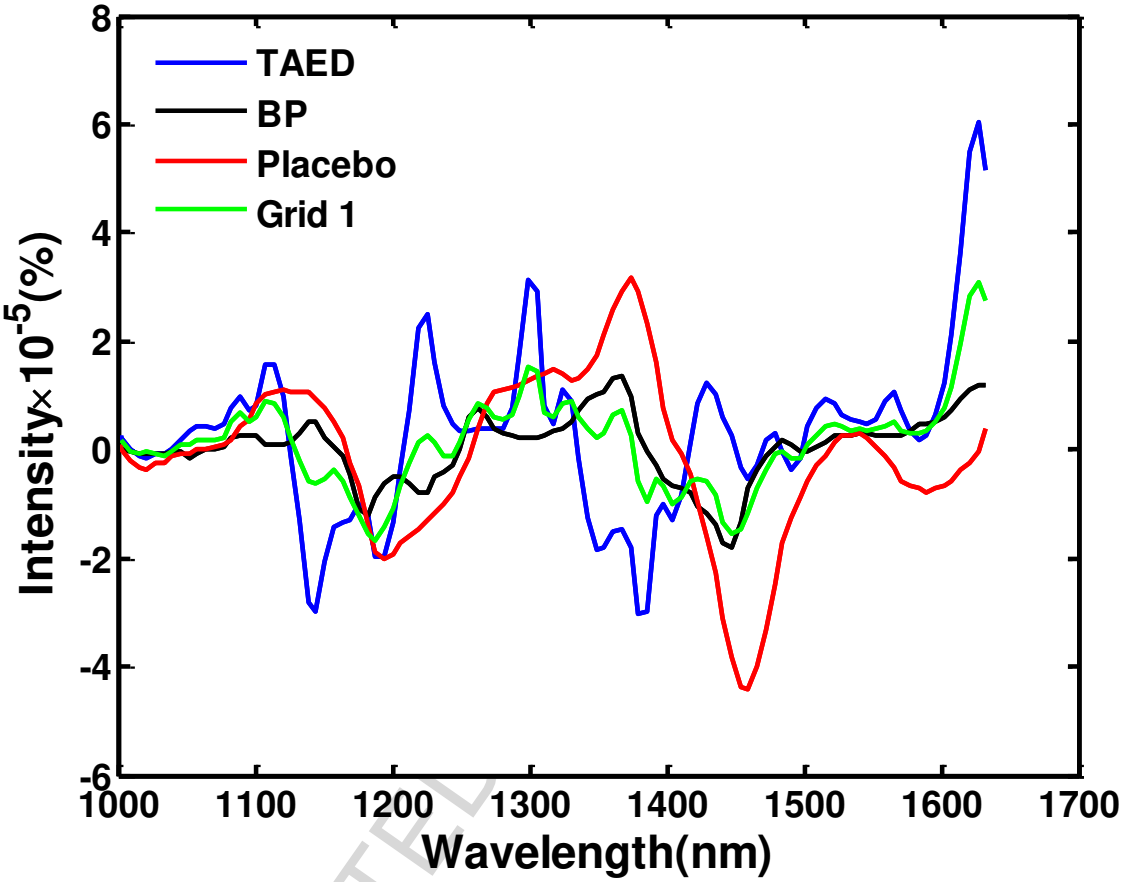

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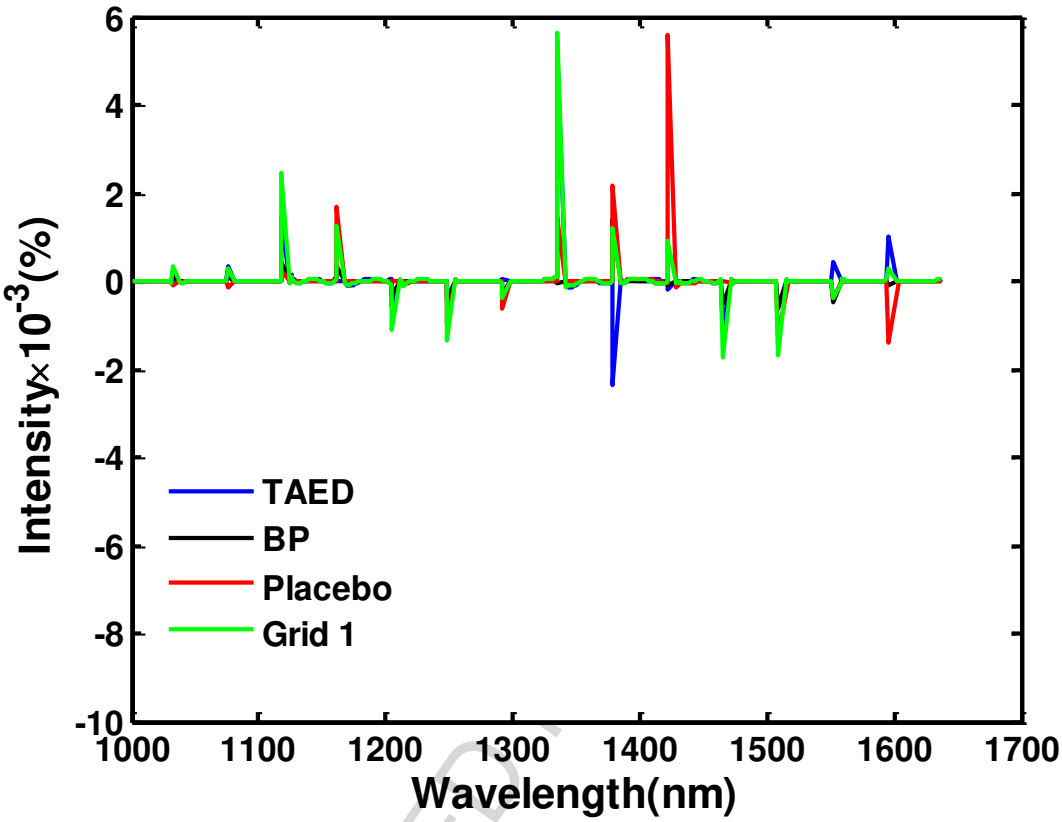


(e)

Fig. 5. Pure components and the mixture spectra obtained by NIR probe using: (a) original reflectance spectra (b) first derivative, (c) second derivative (d) second derivative of Norris-Williams method (m=6) and (e) second derivative of Savitzky-Golay method at P=6 and m=7.

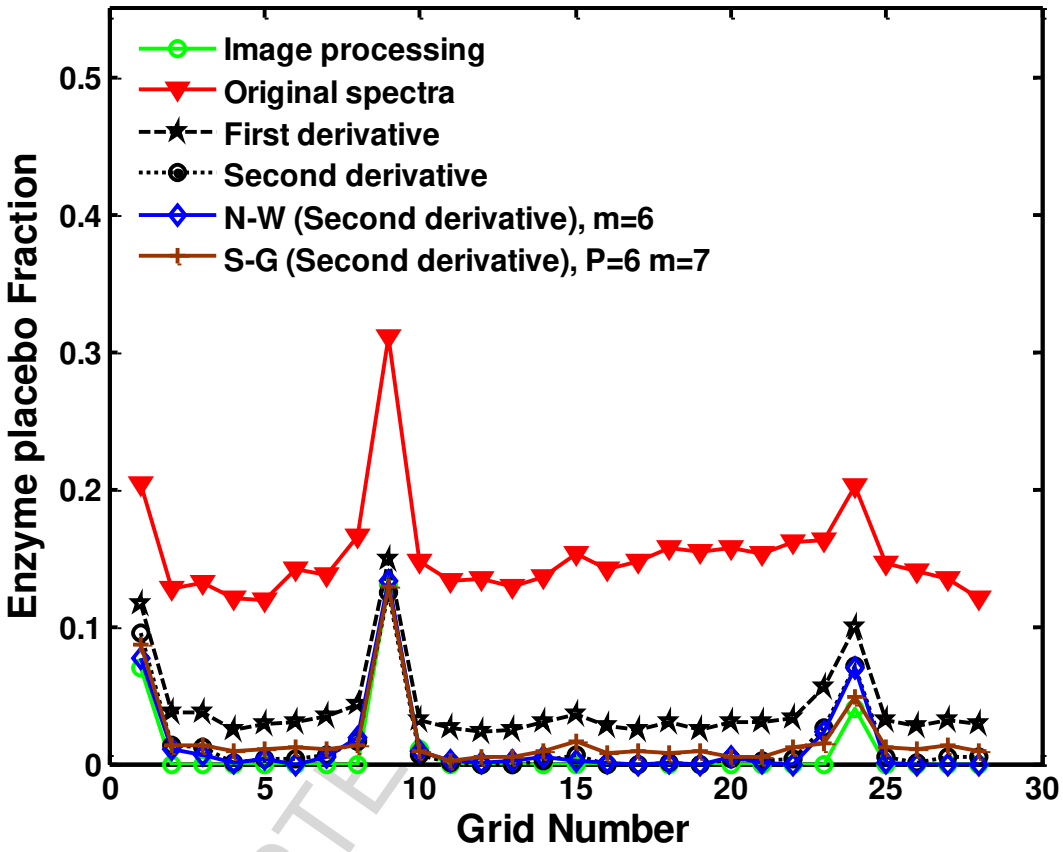
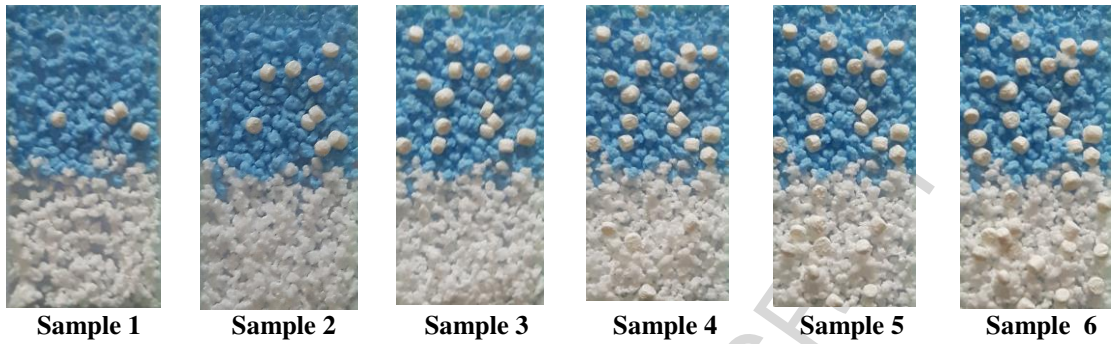
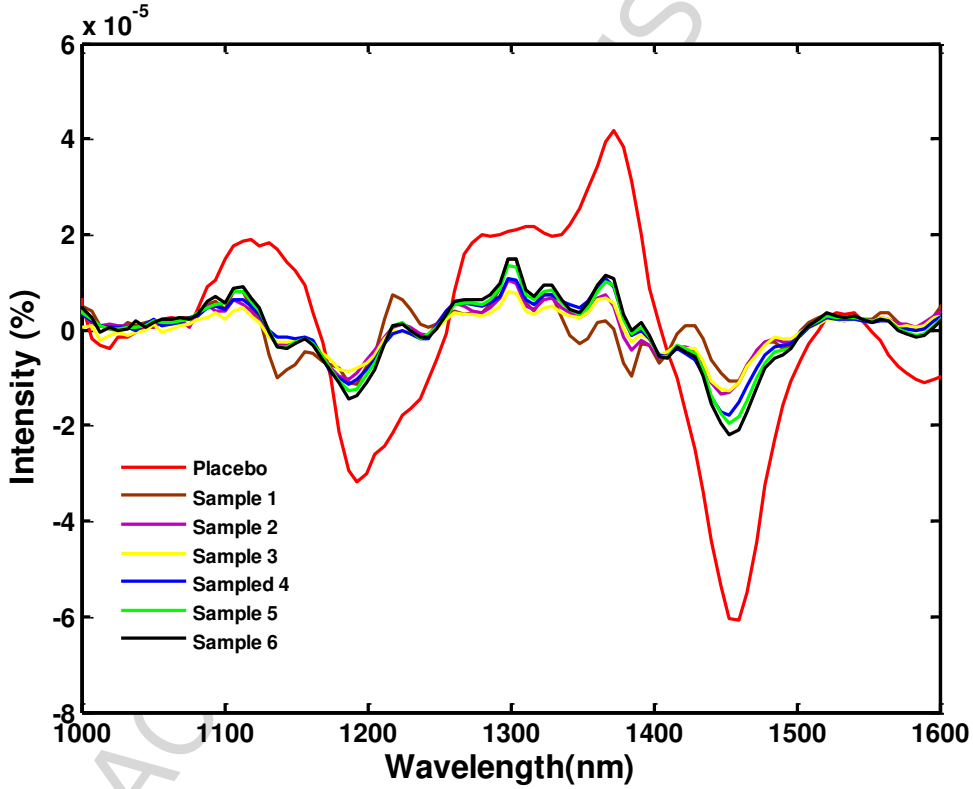


Fig. 6. Enzyme placebo fraction in ternary mixture obtained by image analysis, original reflectance and different pre-processing methods.

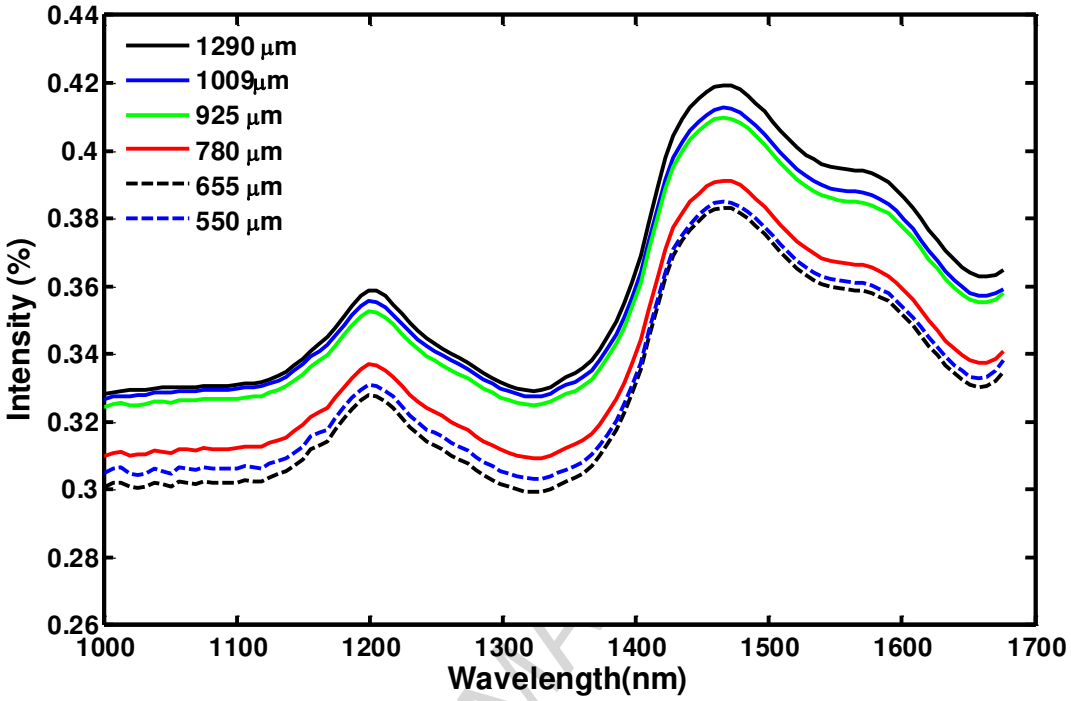


(a)



(b)

Fig. 7. (a) Gradual addition of enzyme placebo granules on the bed of TAED and BP, (b) spectra viarition between different samples (obtained by second derivative of Norris-Williams method (m=6)).



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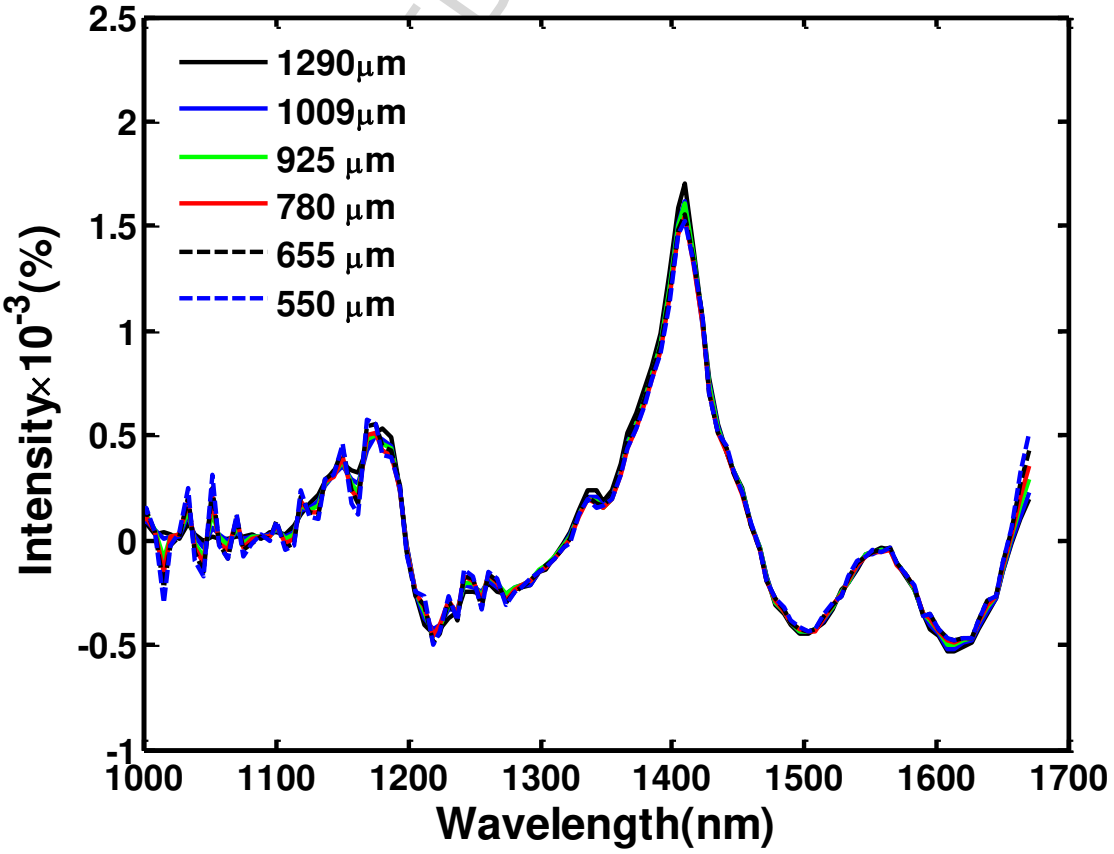

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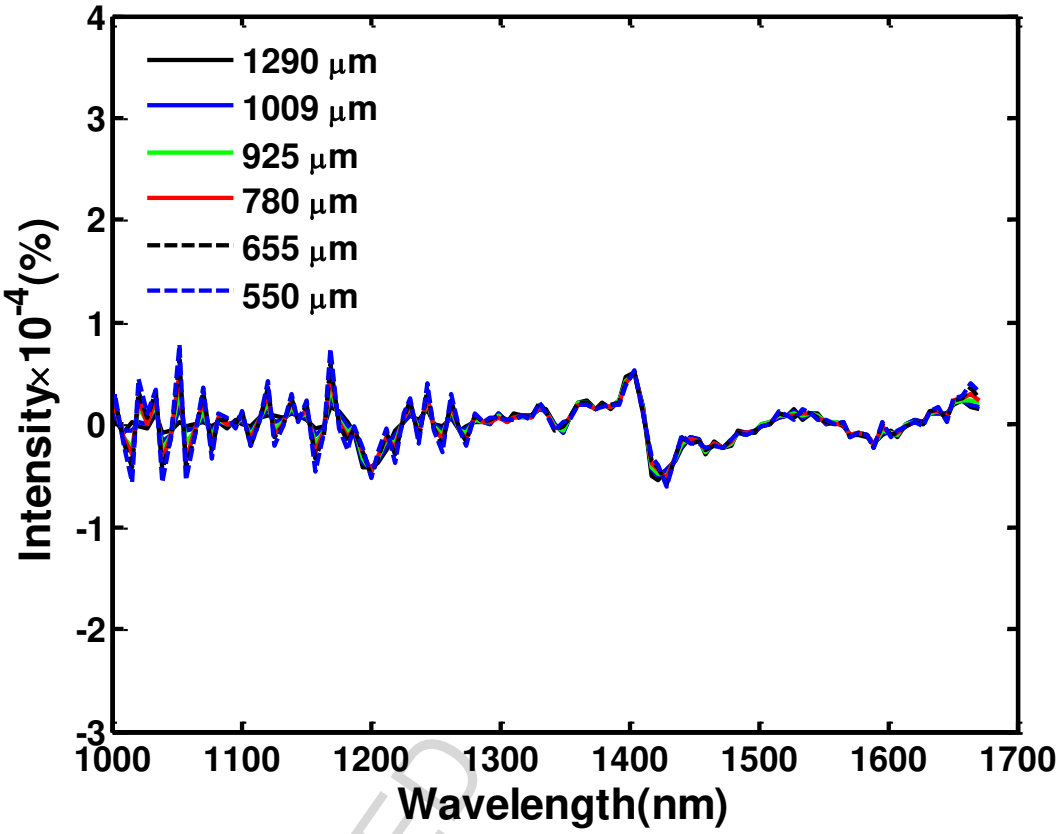
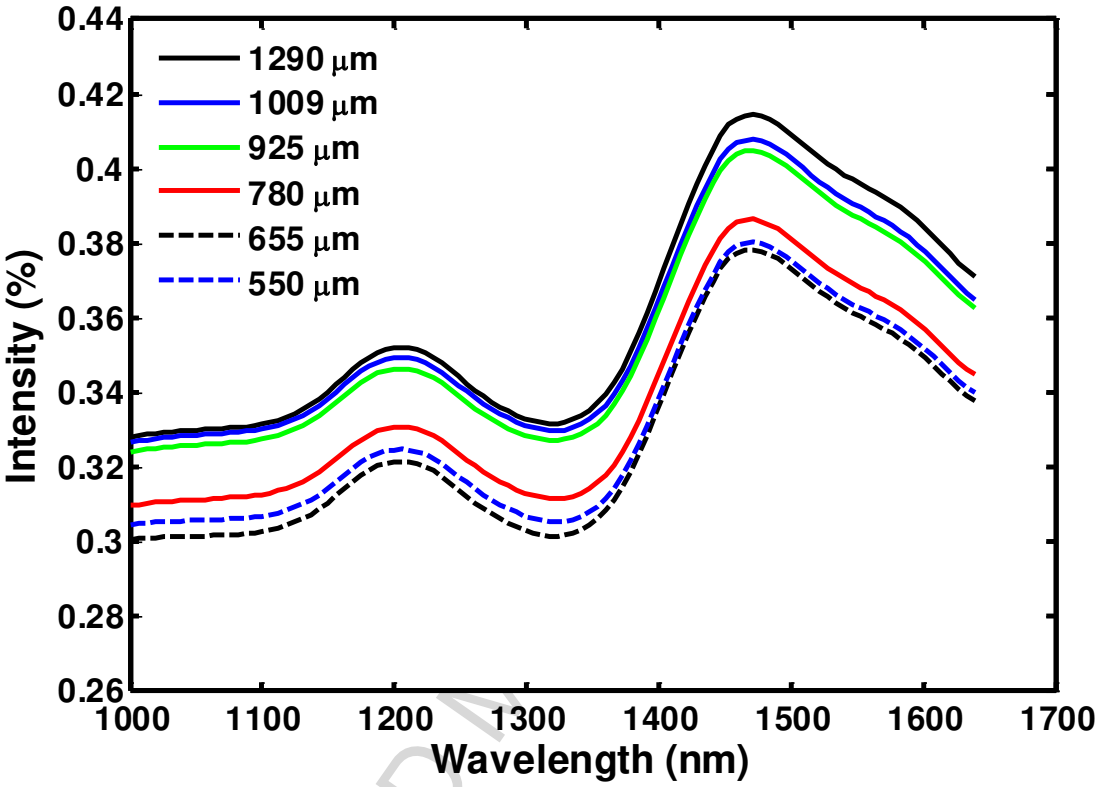
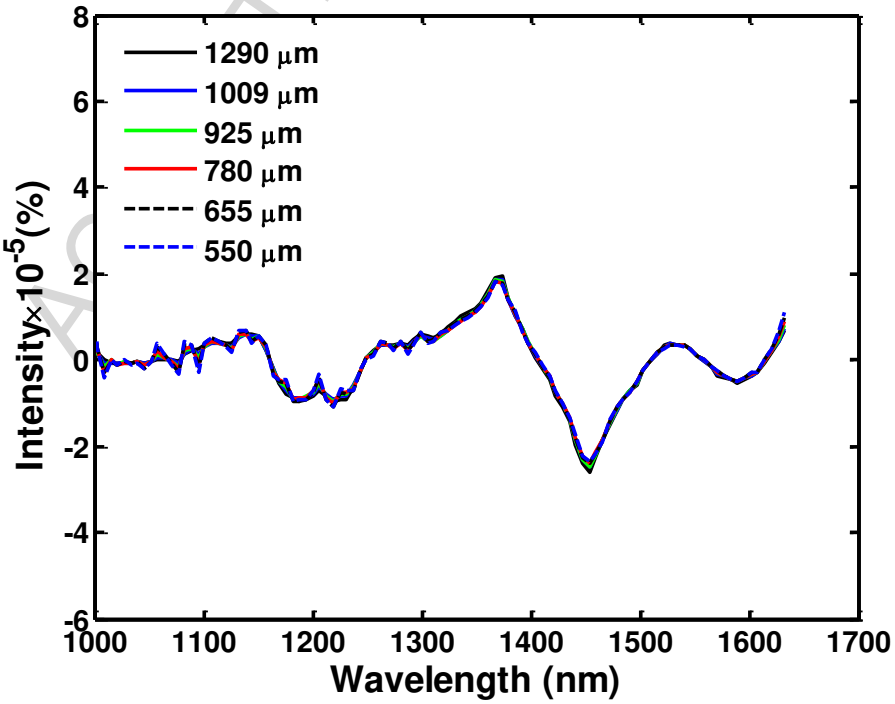


(c)

Fig. 8. (a) Original reflectance, (b) first and (c) second derivative spectra of different sieve sizes of enzyme placebo granules (1290, 1009, 925, 780, 655 and 550 μm).

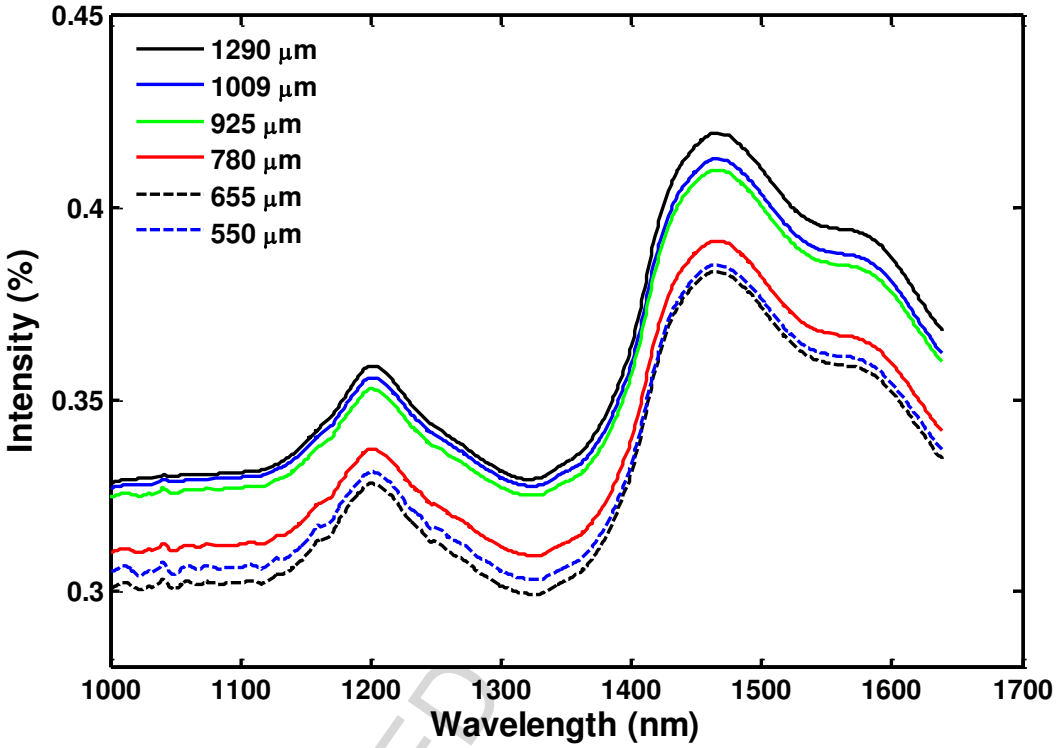


(a)



(b)

Fig. 9. (a) Norris-Williams spectra of original reflectance and (b) second derivative of Norris-Williams spectra (m=6) at different sieve sizes of enzyme placebo granules (1290, 1009, 925, 780, 655 and 550 μm).



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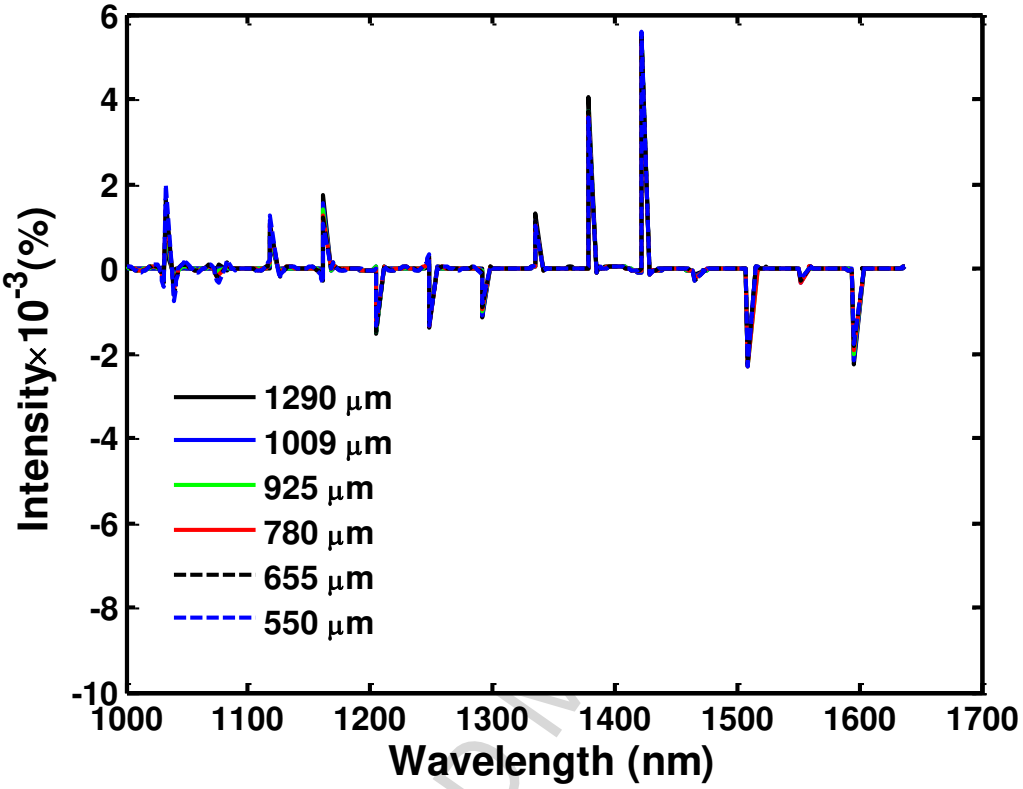


(b)

Fig. 10. (a) Savitzky-Golay spectra of original reflectance and (b) second derivative of Savitzky-Golay spectra (P=6 and m=7) at different sieve sizes of enzyme placebo granules (1290, 1009, 925, 780, 655 and 550 μm).

1-Unsegmented heap **2-Inserting vertical blades** **3-Inserting horizontal blades**

(a)

(b)

Fig. 11. (a) Different stages of sample extraction in ternary heap (b) grid marked heap.

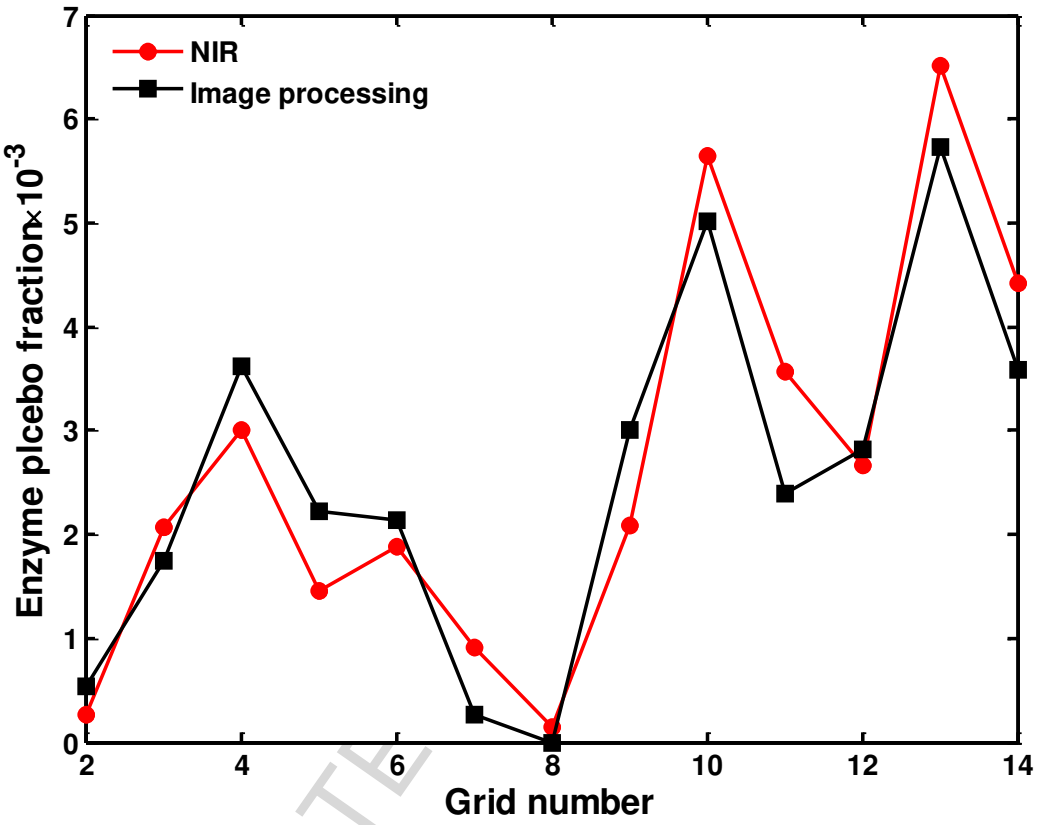


Fig. 12. Enzyme placebo fraction for the ternary heap of laundry detergent powders obtained by the proposed NIR technique and image processing.

Table 1: $MAE_{overall}$ results using original reflectance, SNV, first and second derivative methods.

Mode		Original Reflectance	SNV	First Derivative	Second Derivative
$MAE_{overall}$	**Binary mixture**	0.1675	0.1598	0.1302	**0.1297**
	Ternary mixture	0.9194	0.6049	0.1830	**0.1731**

Table 2: $MAE_{overall}$ results of Norris-Williams method.

	Mixture	Mode	m						
			1	2	3	4	5	6	7
$MAE_{overall}$	**Binary**	**First Derivative**	0.1376	0.1342	0.1324	0.1339	0.1374	0.1418	0.1460
		Second Derivative	0.1269	0.1289	0.1266	**0.1245**	0.1250	0.1302	0.1330
	Ternary	**First Derivative**	0.1822	0.1818	0.1845	0.1942	0.2195	0.2587	0.3107
		Second Derivative	0.1749	0.1774	0.1760	0.1736	0.1713	**0.1673**	0.1721

Table 3: $MAE_{overall}$ results of Savitzky-Golay method.

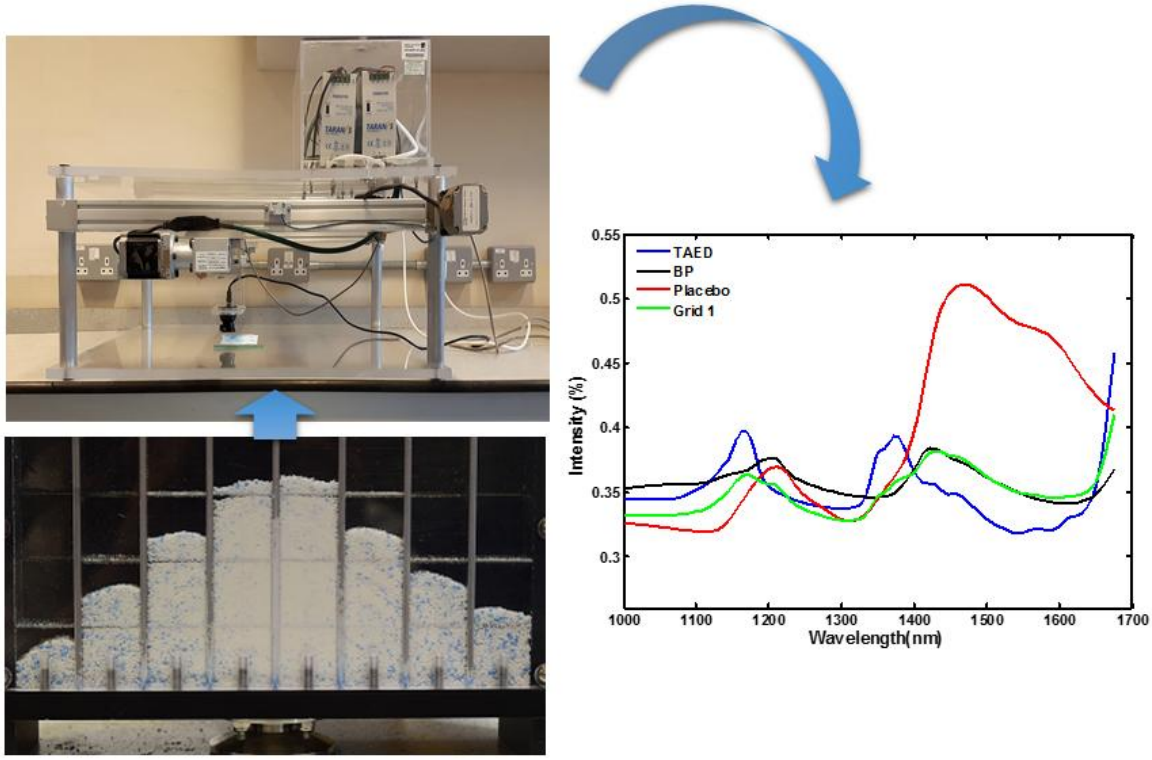
Polynomial order (P)	Number of points (m)	$MAE_{overall}$ (Binary mixture)		$MAE_{overall}$ (Ternary mixture)	
		First Derivative	Second Derivative	First Derivative	Second Derivative
2	3	0.1350	0.1389	0.2481	0.1909
	5	0.1450	0.1231	0.2501	0.1898
	7	0.1295	**0.1184**	0.2499	0.1725
	9	0.1258	0.1509	0.2473	0.2133
3	5	0.1439	0.1238	0.2506	0.1906
	7	0.1294	0.1231	0.2493	0.1743
	9	0.1285	0.1494	0.2487	0.2594
4	5	0.1286	0.1230	0.2505	0.1902
	7	0.1306	0.1199	0.2506	0.1713
	9	0.1286	0.1472	0.2492	0.2525
5	7	0.1306	0.1215	0.2513	0.1719
	9	0.1286	0.1480	0.2487	0.2541
6	7	0.1298	0.1229	0.2510	**0.1643**
	9	0.1285	0.1475	0.2497	0.2557

Table 4: Effect of SNV method followed by different derivatives on the component fraction of binary and ternary mixtures.

	Binary mixture				Ternary mixture			
	SNV+first derivative	**SNV+second derivative**	**SNV+ Norris-Williams derivative**	**SNV+ Savitzky-Golay derivative**	**SNV+first derivative**	**SNV+second derivative**	**SNV+ Norris-Williams derivative**	**SNV+ Savitzky-Golay derivative**
$MAE_{overall}$	0.2036	0.2099	0.2082	0.2215	0.4488	0.2943	0.2785	0.3186

Table 5: Error results of individual components.

Mixture	Error	Components	Mode				
			Original Reflectance	First Derivative	Second Derivative	N-W, Second derivative	S-G, Second derivative
Binary	MAPE	TAED	17.66	12.80	11.27	11.33	10.91
		BP	16.13	13.21	11.74	11.51	11.02
Ternary	MAPE	TAED	55.01	13.98	15.46	14.68	13.89
		BP	46.27	12.00	13.93	13.82	13.53
	$MAE_{placebo}$	placebo	0.1436	0.0322	0.0065	**0.0047**	0.0092



Graphical abstract

Highlights

- Segregation of low content level ingredient in detergent powders is quantified by NIR
- The second derivative of Norris-Williams method is the best pre-processing technique
- Low level enzyme placebo granules can be highly segregated in washing powders heaps