
Review of New Segregation Measurement Technique

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Abstract

Segregation in industrial settings is responsible for a significant amount of lost product due to poor quality issues. In the pharmaceutical industry, segregation of the active ingredient is a critical problem that can lead to loss of life or physical harm if not closely monitored and controlled. Therefore, finding a way to control or predict segregation is critical to optimizing product design or to mitigate quality issues with bulk powders and granules. Obviously, the best way to handle segregation is to create a product consisting of a mixture of key ingredients that does not tend to separate when subjected to typical stimulus in handling processes and distribution networks. While this is the best alternative, it is often difficult to fully achieve in practice. One of the needs to accomplish this goal is to find a method of easily characterizing a mixture to measure segregation potential. This paper addresses that need. It describes an automated methodology used to measure segregation and evaluates that method for consistency, repeatability, and correlation to previous methods. The method first forms a pile of material in a controlled manner and then uses reflectance spectrum to differentiate between components in a mixture along the pile. The method of computing the concentrations and segregation intensities from reflectance measurements is presented. Repeat experiments are done to determine the expected error of the method. This error is found to be within 7% from test to test for a badly segregating material and within 0.5% for a moderately segregating material. The method also uses a complex data acquisition scheme and numerical analysis of large amounts of data. We measured the error of the data collection and subsequent numerical analysis and found the error for computation to be within 0.3%. We compared this to other manual methods and found good correlation to these methods of segregation measurement generating data within 7.8% of other methods.

Key words: Segregation, Spectral analysis, product quality, quality by design

Introduction

Currently, the pharmaceutical industry relies on one of two formulation routes to mitigate segregation of granular feed stocks. The first methodology is dry blending and is by far the simpler route. In dry blending, individual ingredients are mixed to form dry blends which are packed into tablets and capsules. The second methodology is wet granulation. In wet granulation, raw ingredients are combined with liquid, granulated to form large sized particles, dried to remove binding liquid, sized to assure quality product, and packed in tablets and capsules. There is almost always a recycle step in a wet granulation phase which complicates the process and batch inventory management. In addition, wet granulation can cause unwanted reactions that affect drug quality. Dry blend is simplest, but more prone to segregation. Wet granulation is more costly and complex, but less sensitive to segregation. If possible, pharmaceutical companies will choose the simpler process. Therefore, a tool to determine the potential segregation problems of dry blends is needed. The methodology presented in this paper addresses the specific need in typical dry blend processes and it is hoped that the tool and methodology can be extended to potential segregation measurement in wet granulation processes as well. In addition, the tool and method described can be applied to the food, chemical, cosmetic, paint, powdered metals, and ceramic industries.

Segregation is a mechanistic phenomenon. Therefore, it is useful to understand the magnitude of segregation, measure the pattern, and if possible infer the cause. Segregation is also a multi-component phenomenon where one component may have one or several causes of segregation. For this purpose, a small review of some of the causes of segregation may be instructive. The following is a short list of some common segregation mechanisms:

Sifting

Fines may sift through a matrix of coarse particles during handling. This mechanism requires that the void space between adjacent particles be large enough to permit fine particle to pass through. Generally, this requires a particle size difference of about 3:1 [1]. Inter-particle motion is also required to provide a means of exposing empty voids spaces to fine particles [2]. The fines must also be free flowing enough to prevent arching between adjacent particles and the void spaces must be empty enough to accept fine particles [3]. In general, this type of segregation produces a radial pattern as material forms a pile in process equipment [4]. The fines accumulate near the pile charge point and decrease in concentration toward the edge of the pile.

Angle of repose differences

Two materials may have different angles of repose. Thus, when these two materials flow down a pile they essentially create overlapping piles where the material with the steepest repose angle accumulates near the top of the pile while the material with the flattest repose angle accumulates near the pile edge [5]. Generally, there is a distribution of these two materials along the pile's surface. Repose angle differences of about 2 degrees can result in significant segregation [2]. Material of different particle sizes can possess sufficient difference in repose angles to cause this type of segregation. However, particle size difference is not a prerequisite angle of repose

segregation and materials of the same size can separate via this mechanism. In addition, your process must also generate piles during handling or processing to cause this type of segregation.

Air entrainment

The mixture may contain fines that are small enough to be carried by air currents in the handling system [6]. These fines drop out of the air stream when gas velocities decrease below the entrainment velocity. This causes separation of fines and coarse in handling systems. The fines generally deposit near the container walls. This type of segregation requires a source of air currents in process equipment. This source of air can come from free fall of a compressible material. When the falling stream impacts the material level, the entrained air is pushed out of the interstitial pores and carries the fine particles in the resulting dust cloud. This segregation typically causes a radial pattern during pile formation, but the fines are at the bottom of the pile and not the top [2].

Impact fluidization

If the mixture is fine enough, then air trapped in the interstitial voids can cause material to fluidize. As a large particle drops into this fluidized layer, momentum causes the large particles to penetrate this fluid layer, resulting in a top-to-bottom segregation of fine and coarse particles [2]. This mechanism requires a source of air and the ability of the bulk material to hang onto entrained air for a moderate amount of time.

Any materials can separate due to any difference in particle scale properties provided that the handling system can induce a stimulus that enhances that type of particle separation. For example, surface friction differences can cause angle of repose segregation, but only if piles are formed in process equipment. The fall height and material flow rate change the amount of entrained gas in the material and strongly influence air entrainment. But, this will only be important in a process that is subject to large free fall distances. This suggests that any viable segregation tester must have the ability to vary both feed and pile formation conditions to be able to correlate with reality. Some segregation testers inject an arbitrary amount of gas that is often much greater than would be present in any real gravity feed process, and then measure a segregation potential of fines versus coarse based on this stimulus [7]. Such a segregation method has no ability to predict reality. To be valuable, a segregation method should at least approximate the type of stimulus in typical handling processes and provide some means of controlling this stimulus to allow for matching process operations (i.e. the test method should subject the material to the same or similar behavior found in filling containers in typical systems). This then becomes the first judgment criteria for a viable segregation methodology.

Another need is to have a segregation method that can measure more than just two components. Real mixtures are comprised of multiple components. Current segregation analysis methods focus on measurement of just two components, typically fines and coarse [8] [9] [10]. The tool and methodology presented and reviewed in this paper will consider simultaneous segregation potential measurement of a mixture comprised of up to 6 components. This limit is somewhat arbitrary and could be extended to a greater number of components. However, data from

mixtures of up to 6 component has been evaluated at present. Not all available data will be presented here since the goal of this paper is to introduce and validate the robustness of the method. Thus, the ability for the method to be generally applied to more than two components is an important criterion for a robust segregation analysis method.

Another need for any measurement system to be successful is that the method should produce results that do not change and are consistent within a reasonable error range. Both the overall calculations in segregation pattern and segregation intensity for each component should be reasonably robust. Thus, robustness and consistency is the third criterion for a viable segregation methodology.

Finally, where possible the new methodology should be compared to at least one previous methodology to assure reasonable correlation. It is not required that the new methodology match exactly with previous methods since each method can give slightly different results. For example, there are dozens of particle size measurement techniques which presumably measure the same thing. However, none of these methods measure precisely the same particle size distribution. The same can be said of segregation potential measurements; the segregation potential measurement from technique to technique will not necessarily fall on top of each other. However, they should be reasonably close. Thus, the final criterion is that the test methodology should correlate with other measurements and at least measure the same trends.

Method and Materials

The new methodology consists of filling a container with a representative sample of product in such a way as to induce segregation similar to what one might find in a typical handling process, then measuring the segregation pattern using an optical technique, and computing the segregation magnitude and intensity from the measured segregation pattern (Figure 1). Each of these criteria will be examined for this new methodology and, where possible, quantitative judgments be made on how well the new test method satisfies the criteria.

Dump material into box and observe the change in color intensity along the pile as measured just below the top surface of the pile (rectangle section).

These changes in color intensity are an indication of differences in either chemical composition or in particle size and can be used to estimate the segregation of key components in the system.

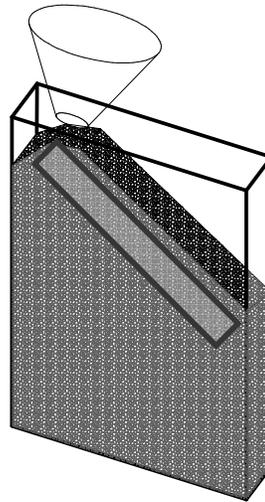


Figure 1. Schematic of segregation tester

The following basic procedure was used to measure the segregation pattern of multi-component mixtures. Only the general steps are presented here; the details of each step are found below as well as details of the calculations required.

1. Feed the mixed material into the segregation slice model bin at a controlled flow rate and preset fall height (as discussed above).
2. Record the top position of the pile and the bottom of the pile (see Figure 3).
3. Determine the active measurement zone by taking measurements of the mixture parallel to the pile and at a depth of 6 mm from the top surface (see Figure 3).
4. Record the overall average concentration of key components in the mixture.
5. Measure the average spectrum of each pure component in the mixture.
6. Select a view port size for segregation measurements of mixture placed in segregation slice model bin.
7. Select the number of view port areas to examine along the pile and then select the number of spectral measurement points to acquire per view port.
8. Measure the average spectrum of the mixture material in a view port for all the view port areas desired along the pile.
9. Use the spectra of the key components, the overall average concentrations of the mixture, and the spectra of the mixture collected along the pile to compute the local concentrations of key components along the pile.
10. Use the concentration profiles to compute segregation intensity numbers for each key component.

While the above procedure is general in nature, the details of each step allow the user to obtain reliable data. The reasons for each procedural choice will be explained so the reader will know what procedural details are important to successful data collection.

The first detail to be considered is control of the filling procedure to mimic or relate to behavior in a typical process. There are two process situations to consider when using segregation test data to predict process behavior. One general case is the static segregation pattern created when a material fills a process container. The second general case is segregation that arises in a dynamic operation condition. For example, does the test data predict segregation that may be present in a rotary shell blender as piles are formed and re-formed? Likewise, does the segregation test data correlate to the particle separation that may occur in a fluid bed?

We will consider the static condition where material free falls into a container at a given rate. Consider what happens in this case from a physics standpoint. A collection of particles falls into a container. These particles tend to spread as they accelerate. They may travel as a stream or they may travel as individual particles. In either case, the falling material entrains air in the surrounding area as it falls. If material travels as a stream, then it impacts the pile at a velocity near that given in equation 1.

$$V_{\max_{pile}} = \sqrt{2 \cdot h \cdot g} \quad (1)$$

This initial velocity free fall velocity depends on the distance of the fall (h). However, if the solid's flow rate is small, then the free fall stream spreads and the velocity of impact depends on the terminal velocity based on air drag (equation 2). In this case, the initial impact velocity is a function of the effective particle size (Dp), density of solid particles (ρ_s), density of the air (ρ_{air}) and viscosity of the air (μ_{air}). The actual impact velocity will be somewhere in between. Velocity increases as per equation 1 until it reaches the terminal velocity in equation 2.

$$V_{\min_{pile}} = \left(\frac{2 \cdot g \cdot (\rho_s - \rho_{air}) \cdot Dp^{5/3}}{15 \cdot \rho_{air}^{1/3} \cdot \mu_{air}^{2/3}} \right)^{3/4} \quad (2)$$

In addition, the impacting material has associated kinetic energy. When material impacts the surface, the surface can compact and deform plastically. If this compaction is excessive, then the strain energy required to accomplish this compression will influence the kinetic energy of the free fall and reduce the velocity. We assume that loss of strain energy due to compaction with typical materials will be negligible. Thus, we deal only with the drag forces slowing the particle free fall velocities. We assume that, when particles hit the pile, they slid down the pile at the velocity compatible with friction angles of material sliding on material. The velocity (V_{pile}) traveling down a pile of length (L) is shown in equation 3.

$$V_{pile} = \sqrt{V_{impact}^2 + 2 \cdot g \cdot L \cdot (\tan(\theta_r) - \tan(\phi)) \cdot \cos(\theta_r)} \quad (3)$$

This velocity depends on the pile slope angle (θ_r) and the effective friction of material flowing down the pile (ϕ). If the friction angle is greater than the pile slope angle, the velocity down the pile slows and eventually stops. In fact, the stopping distance can be computed using the equation above (see equation 4).

$$L = \frac{-V_{impact}^2}{2 \cdot g \cdot (\tan(\theta_r) - \tan(\phi)) \cdot \cos(\theta_r)} \quad (4)$$

For the case of non terminal velocity flow, the distance traveled down the pile is given by equation 5 and shows a linear relationship between distance traveled down a pile and fall height.

$$L = \frac{-2 \cdot h}{2 \cdot (\tan(\theta_r) - \tan(\phi)) \cdot \cos(\theta_r)} \quad (5)$$

This implies a linear scale relationship between drop height and distance traveled on a pile for the process and small scale segregation test hopper for non terminal velocity flow in a process. For terminal velocity behavior, the scale relationship between the lab scale experiment and process geometry can be computed by equation 6.

$$L = \frac{-\min(V_{\max_{pile}}, V_{\min_{pile}})^2}{2 \cdot g \cdot (\tan(\theta_r) - \tan(\phi)) \cdot \cos(\theta_r)} \quad (6)$$

In either case, there exists a scale relationship between the process and small scale segregation test hopper. The simple analysis described above suggests that two main variables, namely free fall height and solids flow rate, are important in scaling between lab and full scale conditions. For terminal flow conditions, some information about particle size will also be required. Therefore, the segregation tester must have, as a minimum set of scale parameters, the ability to adjust both flow rate and fall height. To accomplish this, the tester was outfitted with a vibratory feed system attached to an extendable platform. The position of the feeder can be raised and lowered using this extendable platform. The vibration control can vary the flow rate into the segregation test hopper.

Segregation Measurement Tester

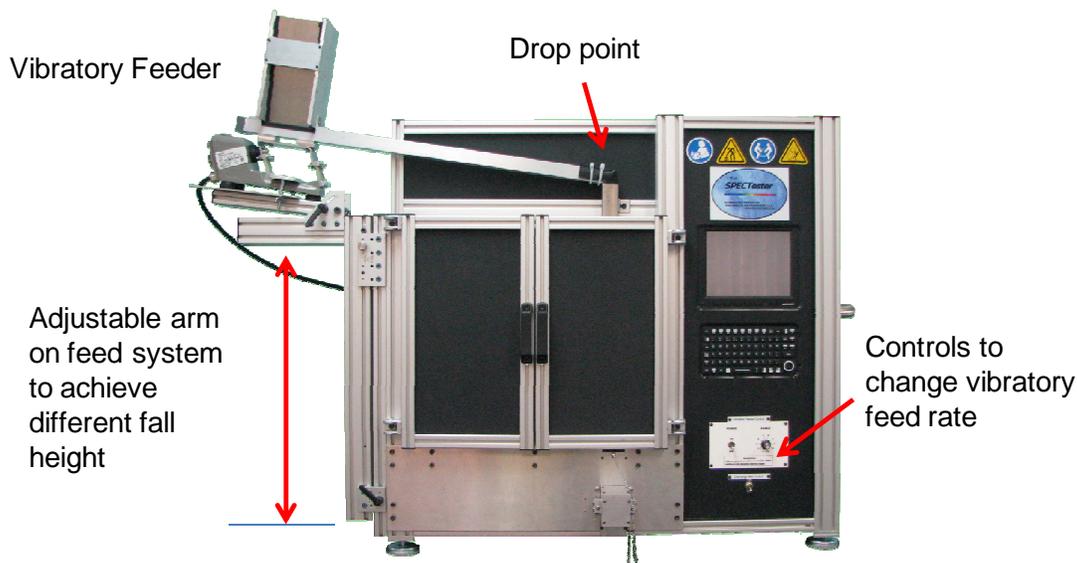


Figure 2. Segregation tester flow control

The second detail involves properly feeding material to be analyzed into the instrument. A feed tube directs material into the slice model to form the pile (Figure 2). The vibratory feeder pan/tube is flat on the bottom, is just as wide as the slice model and directs the flow into the segregation measurement chamber. This is a critical part of the feed design. As material exits the vibratory feeder, it does so in a sheet or solids particle curtain that distributes the particles across the feeder tube and supplies a consistent flow to the entire width of the segregation slice box. This builds the pile without any radial pile effects. The hopper feeder tube is positioned such that the top of the pile formed in the segregation test cell is at one wall of the segregation test cell (Figure 3). The pile surface is a plane that forms on one side of the segregation test cell or slice model. Filling the cell in this fashion produces the same pattern at the front surface of the slice model bin as on the back surface of the slice model bin. Past researchers [11]

discovered that wall effects in slice model bins with powders and granular material require that models be 25 mm or wider to prevent wall induced banding.

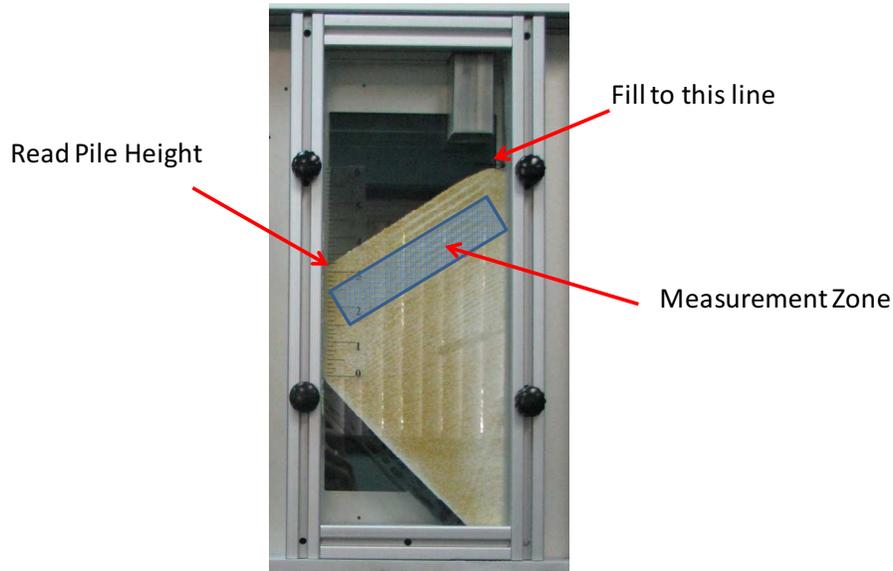


Figure 3. Segregation test hopper

Banding can also naturally occur with slightly cohesive materials as they form a pile. Cohesive materials build up the pile and then periodically cascade down the pile, sifting during the cascade event and producing layers of fines and coarse [12]. This is a natural phenomenon that is part of real systems. Feeding material into the slice model where the walls are close together causes the same banding behavior. The tester must measure real segregation events and not tester induced events. Therefore, the segregation test cell width was limited to a minimum 25 mm to limit the occurrence of banding in the segregation test bin.

The segregation bin measurement zone is positioned parallel to the pile surface at a depth of about 6 mm below the top surface of the pile. The pile is observed through an optical glass plate at the back of the test cell with a standard fiber optic reflectance probe angled at 45 degrees to reduce the spectral reflectance of the glass surfaces. It is assumed that the entire zone parallel to the pile surface is representative of the average material placed in the tester.

It was discovered through trial and error that, for badly segregating materials, segregation may be more prevalent at the end of emptying the feed hopper. This effect occurred in the last 11% of the emptying cycle for material in the feed bin. To assure a representative sample in the segregation test cell, the feed hopper must be filled in small piles to minimize the segregation in this bin. Flow into the tester segregation test cell should be stopped when the level in the feed bin is 30% empty (or to the indicated fill line on the test cell). Thus, we avoided conditions that would cause segregation due to feed bin operation.

To confirm the consistency of segregation from back to front we filled a slice model made of glass end walls with a poorly segregating material and captured an image of the back and front material surfaces to determine how closely these images agreed using standard gray scale image correlation algorithms [13] [14]. We computed the average gray scale as a function of dimensionless radius from the top of the pile and used this data to compute a regression coefficient. The computed regression coefficient for this analysis is $r = 0.971$ ($r^2 = 0.942$) which suggest that 5.7% of deviation between these curves is due to random uncontrolled events and 94.3% of the deviation is due a linear relationship between these curves. A regression coefficient of 0.971 is a strong positive coefficient, suggesting that Figure 4 shows reasonable agreement between the front and back segregation profiles and providing evidence that the controlled feed method and observation of the side of the pile can relate to segregation in real systems as the pattern measured on either side of the segregation test cell is effectively the same. We must still prove that observations measured at the side correlate well with volume based concentrations measured across the test cell. Additional evidence is presented below when segregation profiles measured with the new test technique are compared to alternate manual segregation test measurements incorporating the concentrations based on volume in the test cell.

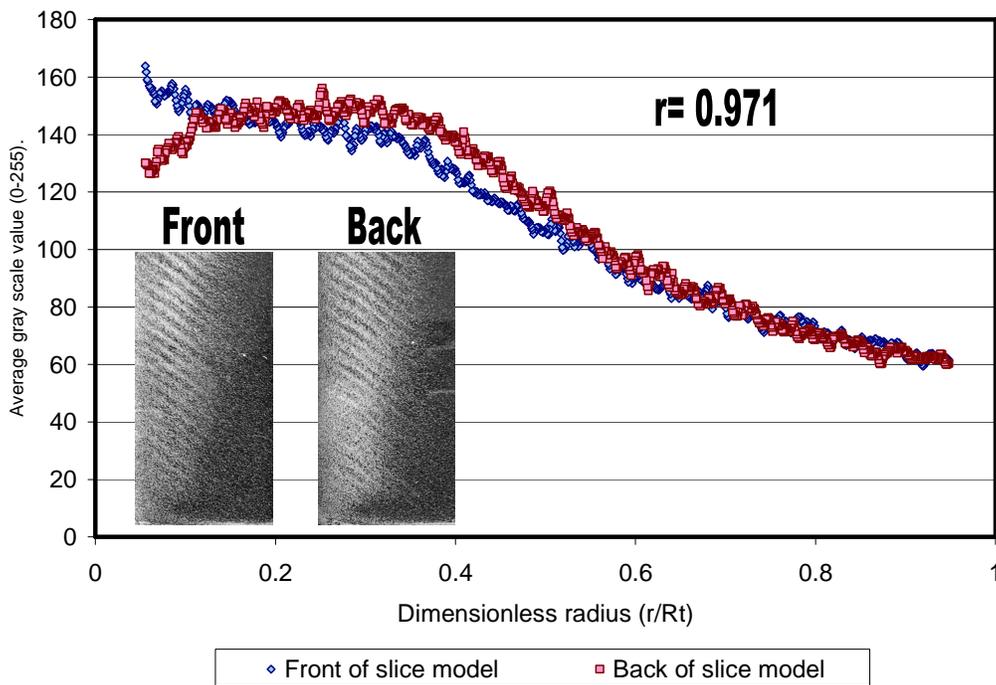


Figure 4. Correlation between front and back segregation pattern

Controlling flow behavior into a slice model, along with the ability to control both the feed rate and drop height, suggests that the segregation tester can be tuned to approximate process fill behavior. The data from this tester should also have applicability in dynamic segregation where segregation in blenders that form piles or inter-particle shear takes place. However, this test technique may not have applicability to conditions where the bulk material is fluidized and

segregation is caused by the act of fluidization. The current filling methodology must be modified to accomplish this task.

The next detail in the methodology is to measure reflectance spectra of the mixture along the pile and the pure components and use this data to compute the concentration profile of key components down the pile. However, a discussion of the theory behind these measurements and calculations will prove useful.

Theory/calculation

Multi-component Segregation Theory and Measurement

To be of value, the measurement technique must be able to quantify segregation patterns for more than two ingredients. Literature is full of examples and theories outlining the segregation of bimodal mixtures. These measurements and the theories developed from these measurements are over simplified. If the component of interest does not deposit in one location, then another component increases its concentration to make up the difference. When three or more components are added to the mix (multi-component) the situation becomes much more complex. It is possible that two components segregate relative to each other, but adding additional components expands the potential interactions significantly. Theories describing this complex situation must allow for this possibility. Likewise, the measurement technique must be able to easily measure the segregation pattern of three or more components. If the subject of segregation modeling is to move forward, the measurement of multi-component segregating systems is at the heart of the discovery process. The author's contention is that sometimes the modeling leads the measurement, and other times the measurement leads and points the direction for the mathematical modeling. However, both are required in order to make significant forward steps in understanding a scientific topic. Very little is being done in the area of multi-component segregation theory largely due to the lack of an instrument capable of easily measuring segregation potential of multi-component systems. The following analysis presents a general method of measuring multi-component segregation potential. Several assumptions and simplifications have been made as a means of making the calculations and measurement simpler. At the heart of these measurements are the evaluation and use of reflectance spectra. The examples presented in this paper to validate the technique use reflectance spectra in the visible as well as near infrared (NIR) wavelengths.

A basic discussion of reflectance spectral measurements may be useful to the reader. If diffuse light of a given wavelength shines on a sample of particles, all at a known distance from the probe, the intensity of the light reflected back depends on three primary interactions. First, the particles can disperse the light based on simple light scattering. In this case the brightest intensity is caused by the finest particles. Second, if the particles contain colored pigment or chemicals that preferentially absorb a given wavelength of light, then the light being reflected back is only that which was not absorbed by certain pigment or chemicals. A surface looks red because all light hitting the surface except the red light is absorbed. The intensity of a reflectance spectrum, then, is a function of the chemical and pigment makeup in the measurement zone. Finally, in some cases, light absorbed activates bond in a particular

chemical, absorbing photonic energy and converting it into photonic energy of a different wavelength. This is the basic principle involved in fluorescence. The analysis presented assumes that fluorescence is not a major effect in the systems studied. Thus, intensity of a reflectance spectrum is a function of the particle size and the pigments or chemical in the observation zone.

A reflectance spectrum also depends on the distance to the target. Non-laser light expands at some angle as it emits from the source. The intensity of the light reaching the target depends on the distance from the source and follows an r square law. When light hits the target it is usually reflected back in a diffuse manner. Thus, not all of the reflected light is captured by the reflectance probe, even if none of it is chemically absorbed

Consider the case of a powder material surface placed against an optical glass plate. The distance to target depends on the position of the particle surface relative to the plate surface. The probe may be at a prescribed distance from the optical plate, but the target is the particle on the other side of the plate. If the light shines on the particle directly against the plate, then the intensity of light is a maximum value. If the light hits a particle between the voids of the particle pressed against the plate, then the intensity of the reflectance spectrum is lower. When measuring a reflectance spectrum of a powder there will be variations in spectral intensity due to particle size distribution effects. A single reflectance measurement is not sufficient to determine the average reflectance spectrum of the powder. Therefore, we must average multiple spectra to obtain a representative spectrum value.

An integral part of the measurement process using this technique is the basic assumption that all data collected by spectral measurements is for material that has a known average concentration of key components. Simply put, all spectral data collected – when averaged together – represents the spectrum of a consistent mixture made of the specified concentrations of the key components. These average concentrations (step 4) are required for the calculation of the concentrations in the mixture. They aid in the calibration of the spectral information to convert the measured spectra to concentrations. Correctly identifying the expected concentration of any given component in the mixture is a critical detail.

In step 5, pure components are placed in the component trays in a loose packed condition (Figure 5). Care is taken during this procedure to fill the component trays by scooping material into the tray using side-to-side motion to avoid a single pile in the center of the tray. The object of this filling process is to present to the optical glass a representative sample in terms of particle size. Thus, the trays were filled with minimal segregation. As pointed out above, a single measurement is not sufficient to characterize the average spectrum of any pure component. The probe measurement area is about 2.0 mm and ten measurements are taken at offsets of 1.2 mm to assure some overlap of spectral measurements. All ten spectra are averaged. The averaged spectra represents the spectral fingerprint of each pure component in the system. Care is taken to avoid measurements near the component tray edge or top of the component tray. It is critical that the probe measurement position for the material in the component trays be at the same distance as the measurement position for the mixture. This is done by calibrating the distance between the probe and the optical glass. The final calibration

is done by placing a homogenous reflective surface on the glass in each measurement area (segregation bin and pure component trays areas) and adjusting the intensity of the signal to be uniform at each measurement location.

Fill the component trays

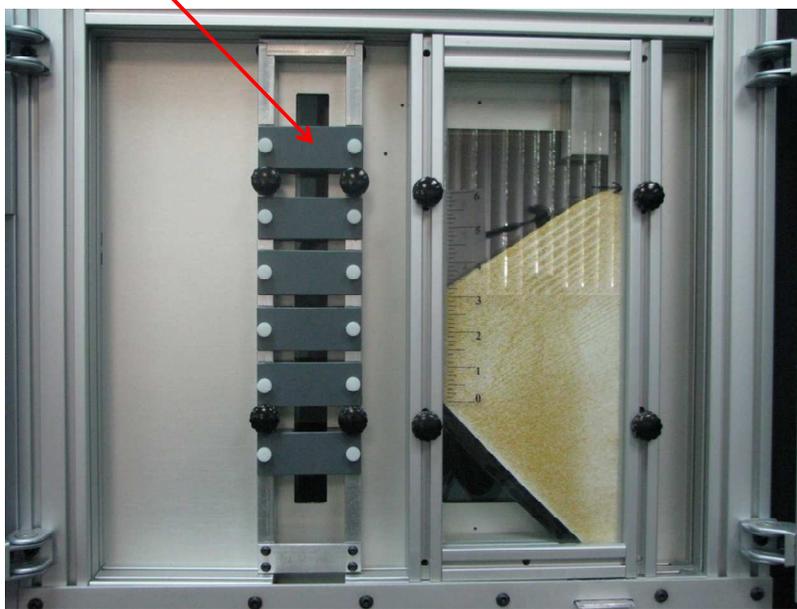
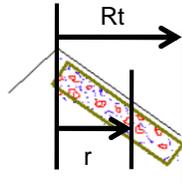


Figure 5. Filling the component trays

Detail six requires identification of the smallest representative size that describes the segregation event(s) with the material of interest. Segregation measurement is a scale issue. The size of the chosen viewport should be large enough to contain a representative number of particles, yet small enough that differences in local compositions are not lost in the averaging scheme (Figure 6). In general, when no clear banding or pattern is observed, then selecting the view port to be at least 10 times the average particle size limits the error between consistent view ports to below 1%. If banding exists, then the view port must be large enough to cover two banding periods. If there is no clear cut way to assign the viewport, then several view ports should be selected and calculations performed using all of the view port sizes. The ideal view port size is found by plotting the segregation intensity factors as a function of viewport size. The measured segregation intensity factors converge to a consistent value when the view port size is large enough (Figure 7). Figure 7 shows that sand with an average particle size of 1500 microns requires a view ports size of about 4500 microns in order to reach a stable segregation intensity. This does not mean the view port must be exactly three times the average particle size because particle size, shape, banding and segregation pattern formation are all reasons that the view port may need to be changed.



Define the size of the view port and measure the spectra along the top of the pile. Adjacent viewports can overlap and tester can measure concentration at up to 50 locations along pile.



Figure 6. Typical measurement zone along pile top surface

Steps 7 and 8 require the acquisition of a spectrum for the mixture at each location of interest. The probe measurement zone is about 2.0 mm in diameter. Ideally, adjacent measurements should touch or overlap. This implies that a 12 mm viewport should have about 36 measurements (six on each side) to assure a good coverage. If the viewport is 10 mm, then 25 measurements (five on each side) would be sufficient. The selection of the number of measurements in each view port is an optimization issue. Larger measurement increments require some acquisition time, but will give a better result. A view port greater than 14 mm would require more than 49 measurements to be averaged to keep the optimal coverage. Taking 49 measurements at 50 locations along the pile requires about 30 minutes to acquire data and perform the required calculations.

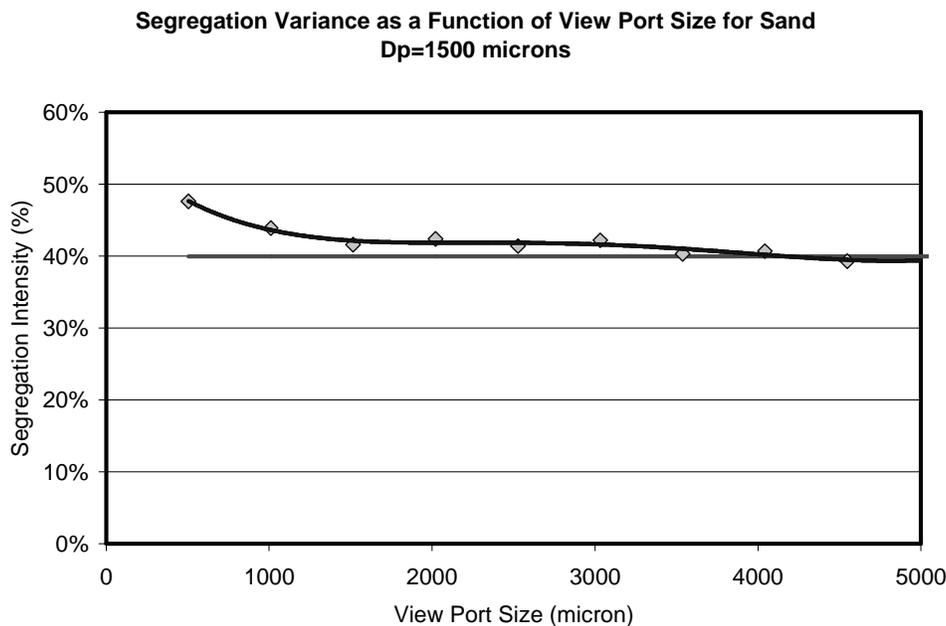


Figure 7. Segregation variance as a function of view port for sand mixture Dp=1500 micron

The next detail involves the decision regarding the type of spectrum used in the mixture analysis. This ninth step requires a spectral mixing law sufficiently general to be used for all types of materials.

One option is to use the complete reflectance intensity spectra, adjusted for black balance, the first derivative, or the second derivative of that complete intensity spectra. The intensity can be scaled relative to another intensity spectrum of one of the pure components. This enhances the differences between the peaks from different components. One advantage of using the second derivative is that the second derivative of the NIR or visible spectra removes most of the spectral information due to particle size and other influences that could affect the spectra intensity. The result is a signal that contains much of the chemical or color difference information with little particle size effects. Even in this case, there is still some influence of particle size and other effects. Thus, we used a spectral mixing methodology that includes the effect of particle size, particle orientation, and the filling of voids between the coarse particles. If the particles were spherical and all the same size, then there would be no optical difference between the particles in the mixture and pure particles placed in the component trays. In this special case, the mixture spectral intensity $FS_{mix_j}(\lambda)$ would be a simple linear combination of the spectral intensity of pure components ($FS_i(\lambda)$) based on the local fraction ($xf_{i,j}$) of each component. However, smaller particles fill the voids between coarse particles, creating a shadow effect for the coarse particles. These fine particles within the voids occupy a proportionally greater percent of area than the volume fraction would suggest. This indicates that a linear combination of pure spectra will not account for the mixture spectra. The mixture spectra will bias toward the fine materials. Likewise, if one component is a flake, then the orientation of particles relative to the glass will determine how much area the spectral probe sees. There are other size and shape effects that can bias the spectral area probe sees for any one component. Instead of creating a robust model to account for all of these potential probe view effects, a weighting factor is added to the additive spectra law to account for the probe measurement area effects. There is a unique weighting factor for each component. In reality this weighting factor is a matrix or tensor because there is a weighting factor for each component and potentially for each particle size. For the purposes of this work, it was assumed that the weighting factors are dependant only on the components. With this simplifying assumption, the spectral additive equation can be modeled by adding a weighting factor for component i (W_i) to the linear combination of spectra (equation 7).

$$FS_{mix_j}(\lambda) = \sum_i W_i \cdot xf_{i,j} \cdot FS_i(\lambda) \quad (7)$$

Equation 7 represents the computed spectrum for the j^{th} position on the pile. There will be one of these equations for every position measured on the pile. An error function (equation 8) was defined as the sum of the square difference between the measured spectra ($F_{mix_j}(\lambda)$) and the computed spectra ($FS_{mix_j}(\lambda)$) for all the spectra measured along the pile.

$$Error = \sum_j (FS_{mix_j}(\lambda) - F_{mix_j}(\lambda))^2 \quad (8)$$

The goal is to minimize the error function given in equation 8. However, there are several other constraints that must be met for the optimal solution to be valid. At each point on the pile the fractional concentrations of the components must sum to 1.0 (equation 9). Likewise, all fractional concentration values must be between 0.0 and 1.0 (equations 10 and 11).

$$1 = \sum_i W_i \cdot x_{f_{i,j}} \quad \text{for all } j \quad (9)$$

$$x_{f_{i,j}} > 0 \quad \text{for all } i \text{ and } j \quad (10)$$

$$x_{f_{i,j}} < 1 \quad \text{for all } i \text{ and } j \quad (11)$$

Finally, the average of all fractional concentrations for each component in the system must equal the total overall mixture concentration (x_{ftot_i}) equation (12).

$$x_{ftot_i} = \frac{\sum_j W_j \cdot x_{f_{i,j}}}{npts} \quad \text{for all } i \quad (12)$$

Equation 8 provides the target optimization function. Equations 9 through 12 provide the equations and constraints to be solved to generate the local concentrations of key components along the pile. All of these equations must be solved together.

Spectral mixing methods used by other researchers fall into one of two categories. Some methods [15] [16] [17] measure the spectrum of the pure compound and store this information in a data base of spectral fingerprints. Cross correlation techniques are used to compare these database spectra to new spectra and the percent of match or correlation between the new spectra and the database spectra indicates the likelihood that the new spectra is identical to a spectra in the data base. If several mixtures of spectra are in the data base, then this method can be used to approximate the concentration of the new mixture by statistical correlation with similar mixtures.

Other spectral mixing methods [18] [19] [20] observe the spectra of a prescribed mixture and focus on variation of spectra with change in one component. The spectra of samples containing various known concentrations of the key component of interest are recorded. Usually, a particular wavelength or band of wavelengths that shows a lot of intensity variation with the component of interest is used to create a least squares curve describing the relationship between the concentration and the spectral intensity. Once this relationship is defined, then the mixture spectrum is analyzed and the intensity in the wavelength band of interest is used to convert the intensity to a concentration of key components. If multiple concentrations are needed, then multivariate least squares analysis needs to be employed to compute the other concentrations from the spectral data.

The reflectance spectral signal is a function of light absorbed by the chemical species and light dispersed or scattered by the particle size of the observed surface. This relationship was first

postulated using the Kubelka-Munk theory [21] [22] of reflectance of films or sheets. The net result is that reflectance is a function of the ratio (K/S) of the absorption coefficient (K) and the scattering coefficient (S). The fact that reflectance is a function of the ratio of these two coefficients complicates the analysis, for one must de-convolute this ratio to take into account the effect of particle size (scattering) and chemical composition (absorption). However, if the system of interest is governed primarily by one coefficient or the other, then a mono-modal relationship will exist between either absorption and reflectance or scattering and reflectance.

Results and Discussion

The tester compares the computed intensity curve with the actual measured curve and adjusts the weighting factors and local fractions at all measured locations along the pile to minimize error between the two curves. In addition, the method used to solve this set of equations is a non-linear least squares optimization with constraints used in NI LabView®. This is a standard solution technique that combines the constraints and data in the same matrix and solves for all of the concentration and weight factors together [23]. It is assumed that the total collected data represent the average material placed in the tester. This provides a method of simplifying the calculations. Normally, an NIR or visible spectral measurement requires that the spectra of several known concentrations of components in a mixture be entered in the NIR or visible unit to act as calibration spectra to “train” the instrument. The spectra of these various concentrations would normally be used to generate a regression plot between concentration and spectral intensity at some key wavelength of light. In this new method the spectra of the pure components and the fact that the overall average concentration is known provides the means of training the instrument. The complication is that all the spectral data is required to compute the concentration data requiring the solution of a very large number of simultaneous equations. The software takes into account all the spectra and then, using least squares correlation techniques, determines the best guess of the concentration of key components. The result is a measurement of concentration of key ingredients along the length of the pile for all measurement points along the pile (Figure 8).

There is not another method that currently measures the segregation profile of multi-component mixtures, so comparison data in the literature is lacking. However, seven mixture systems were studied to ascertain if the segregation pattern was similar to manual segregation patterns measured in similar tests. These manual segregation tests were done by filling a slice model with a mixture, carefully tipping the slice model backward, removing the front plate to expose the material in the slice model, sectioning the top of the pile into 5 or 6 sections and manually measuring the concentrations of key components in each sample collected along the pile. This procedure was repeated for seven different systems containing between two and five components. This manual segregation method was compared to the spectral segregation method described above. The data from the new spectral segregation tester was measured at more points along the pile than could be collected using the manual method. Thus, the data was grouped and averaged over appropriate dimensionless radius values to compute points comparable to the data measured using the manual method. One such data set is presented in Figure 8, describing segregation of three types of bird seed. There is very good agreement between the manual measured points and the concentration points generated from the spectral segregation method.

Based on the complete set of data generated from this validation method, the standard deviation was estimated to be 2.6%. This suggests that the new methodology approximates other methods of measuring segregation with reasonable accuracy, indicating that the spectral method described above can be used to accurately estimate segregation concentration profiles of complex mixtures.

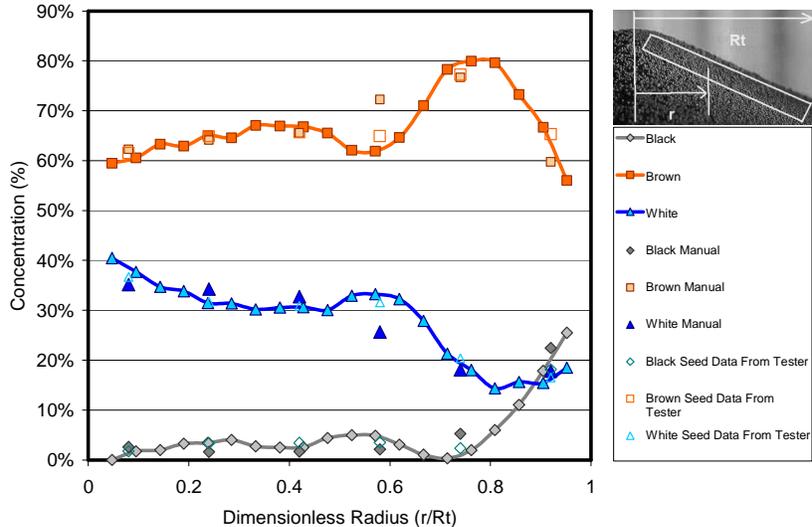


Figure 8. Segregation variance compared with alternate method of measuring segregation for a mixture of three bird seeds

If the measurement method is to be of value, the segregation measurement procedure must be reproducible. Repeatability should be reasonable, even with very easily segregating material. A protocol to test this repeatability sensitivity was done using the segregation measurement procedure outlined above. A set of three free flowing sands of different size and color were mixed. This mixture was introduced into the tester three distinct times and the procedure followed to generate the concentration profiles (Figures 9 and 10). Twenty samples along the pile were analyzed and the deviation off of the average for these three tests was measured. This experiment suggests that, based on a three sigma estimate, the error caused by repeated measurement is about 7.0% for a material that is highly sensitive to segregation. Other data was used with a material that was less prone to segregation and found that the repeated measurement error for that case was 0.5%. Thus the repeated measurement error for this new technique was bound between 0.5% and 7.0%. Figure 10 indicates that there may be some spatial variation effects in the error of the test. However, this could also be due to the nature of the segregation pattern. The data suggests that this spectral segregation test method using controlled filling reproduces segregation patterns with reasonable accuracy.

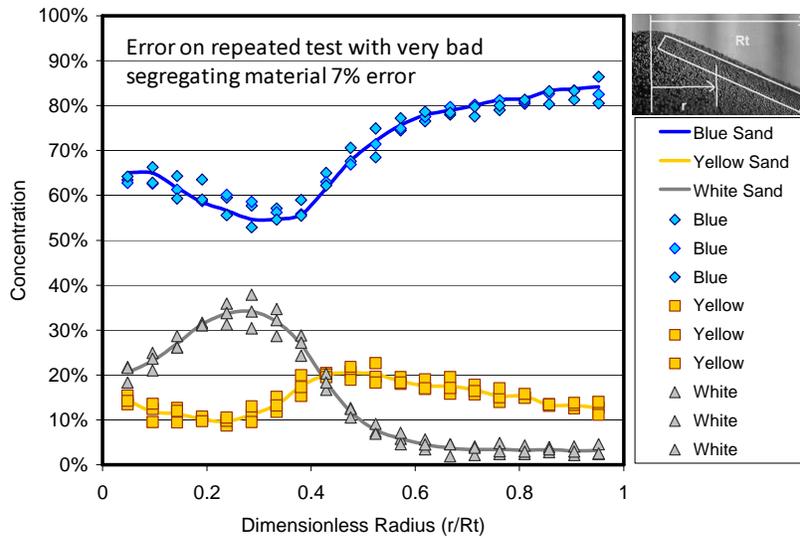


Figure 9. Segregation variance due to repeated tests using spectral segregation measurement

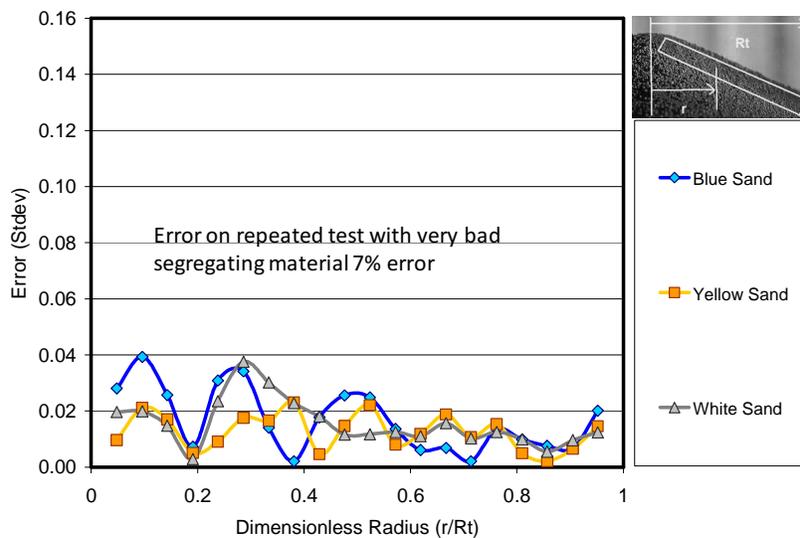


Figure 10. Segregation variance due to repeated tests as a function of radial position using spectral segregation measurement

It is also important that the calculation method used to compute the concentration profiles be reliable. To test reliability, the mixture of three sands was placed in the tester and the concentration profile was measured for this same pattern three times (Figures 11 and 12). The repeated solution of these concentration profiles indicates that based on three sigma deviation, the measurement error for a material that was very sensitive to segregation was 0.3%.

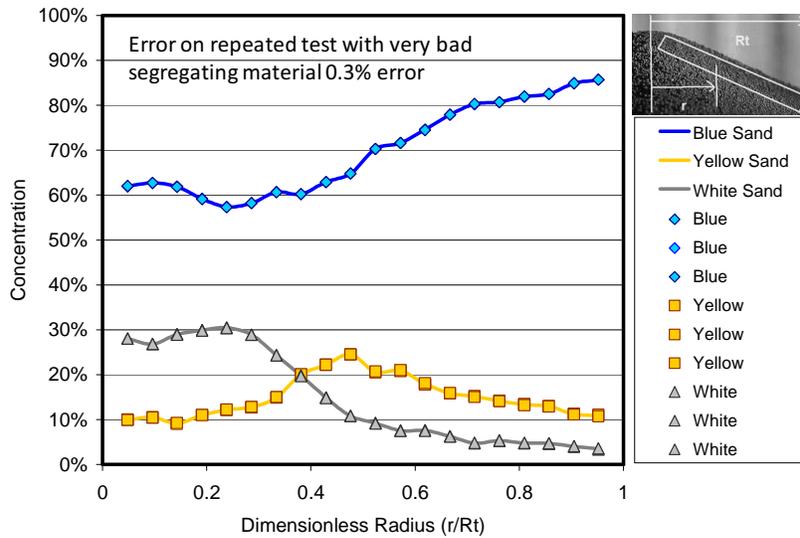


Figure 11. Segregation variance due to repeated calculations of a segregation pattern using spectral segregation measurement

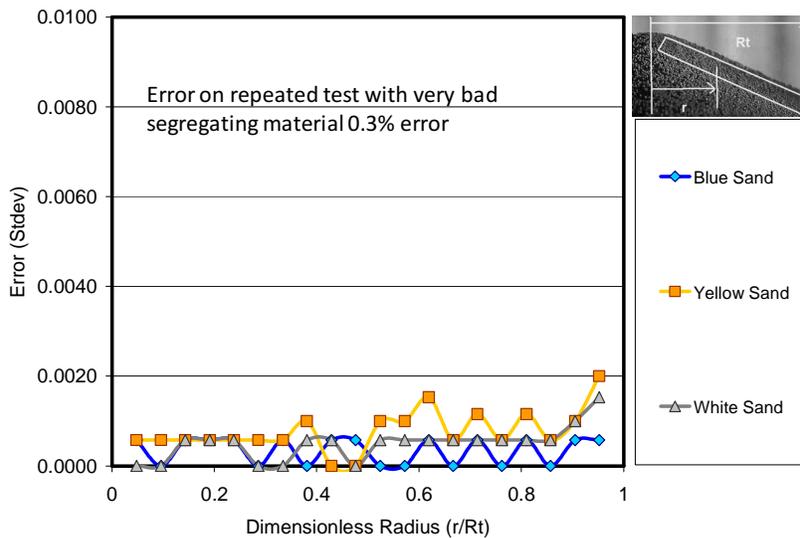


Figure 12. Segregation variance due to repeated calculations of a segregation pattern as a function of radial position using spectral segregation measurement

Conclusions

The data presented suggest that the spectral method described above measures segregation potential reasonably well. The data further suggest that the measuring resolution of this new methodology is limited to about 0.3%. The method cannot resolve concentrations below 1%, but should do a good job with concentrations 1% or greater. Repeatability measurements from test to test are comparable with other methods measuring properties of granular and powder systems such as particle size and shape. This spectral method also compares well with independent analytical methods of measuring segregation, suggesting that it can be successfully used to study segregating materials. To date, nearly 350 systems of different materials have been examined with this new technique using both visible and NIR spectral methods.

The issue that has hampered past study of segregating systems is a focus on bimodal systems. The path forward is to expand segregation modeling to include multi-modal materials. This requires two things: a measurement technique that can measure segregation of these complex mixtures, and the development of theories to facilitate and understand segregation of multi-component material mixtures. Sometimes the measurement leads the theory. Sometimes the theory leads the measurement. One thing is certain: both the measurement and theory are required to push the cause of scientific study forward. It is hoped that this new technique can provide much needed measurements on real systems. Currently, the limitation is a system of 6 or fewer components. However, that limitation is by tester design and not by theory. The calculation for mixtures with more components could be done using this method if the equipment would allow it.

The new measurement method requires between 10 and 30 minutes for up to 50 measurements of six components. Previously, this would have taken analytical labs a couple of weeks to measure. The speed of this new method suggests that formulators can analyze several materials in a single day and use that data to determine or optimize formulations to prevent segregation. The tester has also been used to measure particle size segregation based on a spectral method. However, that will be a subject of another paper. There are aspects of the technique that could be enhanced or fine tuned to create a more precise instrument. However, the analysis of this new segregation method suggests that it can be successfully used to begin a serious study of multi-component segregating systems. The next step will be to use the results from this or similar test technique to develop corresponding multi-component, multi-mechanistic theories describing segregation.

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