Multivariate Statistical Process Control for On-line Monitoring Size of Milling Process

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Abstract— **Ultrasonic attenuation spectroscopy (UAS) is an attractive process analytical technology (PAT) for on-line real-time characterisation of slurries for particle size distribution (PSD) estimation. It is however only applicable to relatively low solid concentrations since existing instrument process models still cannot fully take into account the phenomena of particle – particle interaction and multiple scattering, leading to errors in PSD estimation. This paper investigates an alternative use of the raw attenuation spectra for direct multivariate statistical process control (MSPC). The UAS raw spectra were processed using principal component analysis. The selected principal components were used to derive two MSPC statistics, the Hotelling's T^2 and square prediction error (SPE). The method is illustrated and demonstrated by reference to a wet milling process for processing nanoparticles.**

***Keywords*— Multivariate statistical process control, Ultrasonic attenuation spectroscopy, Principle component analysis, Milling, Particle size,**

I. INTRODUCTION

Manufacture of nano-particulate form products in suspensions is becoming increasingly important to the pharmaceutical, speciality chemical and functional material industries. One of the biggest challenges to nano-processing under industrial conditions has been highlighted as the difficulty in achieving consistency in product quality as characterised by particle size distribution (PSD). On-line real-time characterisation of the product quality properties such as PSD is considered as the enabling technology to tackle the challenges. Among various techniques studied in literature, ultrasonic attenuation spectroscopy (UAS) is considered as one of the most effective PAT techniques for on-line real-time characterisation of PSD for nano-processing [1, 2]. The merits of this technique are that it is non-invasive, non-destructive, can be operated for opaque materials and over a wider size range than a light technique. PSD is estimated from the measured attenuation spectra in comparison with the modelled attenuation spectra. In the measurement part, the attenuation is measured from the ratio of the incident ultrasonic intensity (or amplitude) to the detected intensity along the propagation path at different frequencies, following the equation:

$$\alpha(f) = -\frac{1}{x} 20 \log \frac{I}{I_0} \tag{1}$$

where $\alpha(f)$ is ultrasonic attenuation coefficient (dB/m) at frequency f, x is propagation path (m), I and I_0 are detected and incident ultrasonic intensities (W/m^2). The mathematical models can describe the wave propagating through the medium. The models commonly used for PSD estimation are ECAH [3, 4] and hydrodynamic [1, 5] or coupled-phase [6] models. However, these models are subjected to assumption of relatively low solid concentrations. At high solid concentrations, particle – particle interaction and multiple scattering can occur, but the phenomena were not fully considered in the models mentioned above [7], leading to erroneous PSD estimation. Attempts were made to improve the model for higher concentration by adding parameter to the models as a result the modified models are very complex and difficult to use.

Another issue associated with PSD prediction based on models involves the inverse problem and limitation of working size range. Ultrasonic attenuation models mentioned earlier generate attenuation spectra for a given PSD (forward modelling); and to obtain PSD for a given attenuation spectra, optimisation algorithms have to be applied to minimise the error between the measured and modelled attenuations. This is the inverse problem of modelling, which may generate multiple solutions. The common methods to solve this problem are iteration calculation and advanced technique such as regularisation technique, which call for much time, and the obtained PSD is highly sensitive to noise of the measurement. Moreover, most of the mentioned models work only in the long wavelength regime (particle diameter $a \ll \lambda$), and they might not suit for some particulate processes in which the working size ranges are very wide, 0.01–100 μm, and size changes very fast such as for milling processes.

The above argument leads to the idea of using the raw attenuation spectra directly for process control without the need to estimate PSD. This work investigates the use of ultrasound attenuation spectroscopy (UAS) for developing multivariate statistical process control (MSPC) for processing nanomaterials in slurries. MSPC is a statistical technique applied for monitoring, diagnosing and controlling processes. This technique utilises dimensionality reduction techniques such as principal component analysis (PCA) to extract the most important variables for establishing new variables for process monitoring and control, Hotelling's T^2 and square prediction error (SPE).

II. MSPC MODLE

The proposed methodology of developing multivariate statistical process control (MSPC) models based on ultrasound attenuation spectra (UAS) involves four steps: (1) collection of UAS spectra for monitoring the process under normal operational conditions (NOC); (2) data processing including dimension reduction using principal component analysis (PCA); (3) development of MSPC statistics Hotelling's T^2 and SPE; and (4) application of MSPC method to future process monitoring.

A. Collection of normal operational condition

The first step of the methodology is to collect process data at normal operational conditions (NOC) that is needed to develop the MSPC model. In this application, the recorded ultrasonic attenuation spectra for operations that lead to in-specification product are considered as NOC data.

In the current case, using an instrument UltraSizer MSV, Malvern Instruments, the attenuation spectrum is taken with 50 points per measurement along the frequency range 1 – 120 MHz. With such number of measurement points (variables), MSPC requires a large number of NOC data to yield an effective model. To optimise the measurement points, the required number of the points must retain the information needed for characterisation. For a high-density contrast system, i.e. silica suspension, 8 values of measurements along the frequency range are enough to characterise particle size. For this test, 12 points of attenuation spectrum along frequency range [5 – 100] MHz are chosen. Low frequency (<5 MHz) is not included because of high possibility that the measured attenuation is not accurate [8].

The attenuation spectra were generated at fixed frequencies, [5,10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 100] MHz, which are equivalent to the process variables, and will be treated to reduce the number of variables using principal component analysis (PCA), as will be described below.

B. Principal component analysis

PCA is a statistical technique used for dimensional reduction of a large number of variables, by converting the raw data to some new latent variables. Suppose NOC data set, $\mathbf{X}_{[m\times n]}$ consists of m observations for n variables, PCA processes the data set in the form of linear decomposition as

$$\mathbf{X}_{[m\times n]} = \mathbf{T}_{[m\times n]}\mathbf{P}^{T}_{[n\times n]} \tag{2}$$

where **T** is the score matrix and **P** is the loading matrix. The loading vector is the new axis in which the score of the equation is the quantity of the raw variable projected on the axis **P**. For MSPC model development, it is not necessary to use all of the n variables, and only k variables are observed, $k < n$. Hence the new linear decomposition can be written as

$$\mathbf{X}_{[m\times n]} = \mathbf{T}_{[m\times k]}\widetilde{\mathbf{P}}^{T}_{[n\times k]} + \mathbf{E}_{[m\times n]} \tag{3}$$

where **E** is the error matrix due to the dimension reduction. When the new observations, $\mathbf{x}_{[1\times n]}$, are obtained from the measurement, the score of the new observation, $\mathbf{t}_{[1\times k]}$, can be determined by

$$\mathbf{t}_{[1\times k]} = \mathbf{x}_{[1\times n]}\widetilde{\mathbf{P}}_{[n\times k]} \tag{4}$$

This score will be used as the monitoring variables instead of the original variables. It can be seen in Eq. (4) that only k variables are used.

The combination of scores will be constructed as the one variable which can be used as the monitoring variable. Moreover, the scores are constructed from the dimension reduction, and as a result, error occurs. It is also necessary to monitor this error via the difference of constructed model and original data. The construction of monitoring charts will be described as follows.

C. MSPC Model

The MSPC model uses two monitoring variables, Hotelling's T^2 and square prediction error (SPE or Q-statistic). The Hotelling's T^2 monitoring variable describes the distribution of data around the mean points of NOC data, as defined below

$$T^2 = \sum_{i=1}^{k}\frac{t_i^2}{S_{t_i}^2} \tag{5}$$

where S^2_{ti} – variance of t_i.

The second monitoring variable aims to observe the error between the new models constructed using MSPC and the original data, SPE, defined as follows (sometime is called Q-statistic)

$$SPE = \sum_{i=1}^{k}\left(y_{new,i} - \tilde{y}_{new,i}\right) \tag{6}$$

where $\tilde{y}_{new,i}$ and $y_{new,i}$ are the reconstructed value of the i^{th} process variable from the reference PCA model and the measured value of this variable, respectively.

The confidence limits for both monitoring variables are defined as follows:

$$T^2_{UCL} = \frac{(m-1)(m+1)k}{m(m-k)}F_v(k, m-k) \tag{7}$$

where F_v – F-distribution. Moreover the upper confidence limit for SPE is

$$Q_{UCL} = \theta_1\left[1 - \theta_2 h_0\left(\frac{1-h_0}{\theta_1^2}\right) + \frac{\sqrt{z_v(2\theta_2 h_0^2)}}{\theta_1}\right]^{\frac{1}{h_0}} \tag{8}$$

where θ_i – trace(V^i), V – covariance matrix of error matrix, $h_0 = (2\ \theta_1\ \theta_3)/(3\ \theta_2^2)$ and z_v – standard deviation with confidence $(1 - v)$.

The above constructed monitoring charts are applied for monitoring a wet nanomilling process, as will be discussed later.

III. EXPERIMENTAL

A. *Milling Process Setup*

Fig. 1 shows the experimental on-line milling process set-up, composed of a mixing tank equipped with pH, conductivity and temperature probes and a stirrer. The sample in the mixing tank is driven by a gear pump (Flender) through a stirred media mill (Dyno®-Mill Multilab, Willy A. Bachofen). The sample is circulated between the UAS (UltraSizer MSV) and DLS (Zetasizer Nano) for characterisation and the mixing tank. It was found that the prototype on-line DLS instrument is very sensitive to flowrate; calling for flow control (rotameter, Platon) before DLS to less than 5 mL/min.

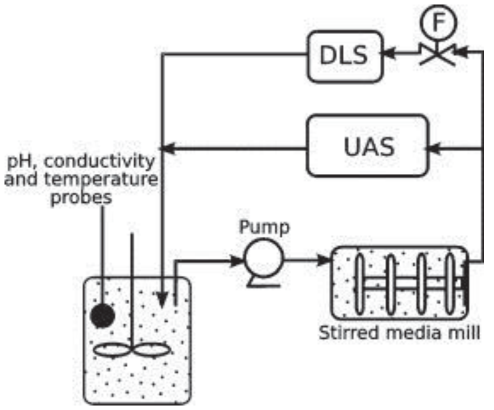

Figure 1. Wet nanomilling process setup.

B. *Materials*

Aluminum oxide (α-Al_2O_3), purchased from Sigma – Aldrich, is spherical in shape (seen under a microscope) with median size (d_{50}) of 107.31 μm, $d_{10} = 67.67$ μm and $d_{90} = 170.97$ μm (measured with MasterSizer 2000, Malvern Instruments). Physical properties of the alumina are as follows: density 4000 kg/m^3, sound speed 10,847 m/s, specific heat capacity 880 J/(kg K), thermal conductivity 35 W/(m K), thermal expansion 8.1×10^{-6} 1/K, shear modulus 124×10^6 Pa and refractive index 1.76.

C. *Operating procedure*

Alumina slurry was prepared for a concentration of 10 wt% (3 vol.%) by mixing the dry powder in 2.5 L distilled water. The slurry was transferred into the mixing tank and stirred for 20 min to guarantee well mixing. Then, the concentrated basic solution was added to adjust the initial pH and conductivity of the slurry (2 mL of NaOH solution increased the pH of the slurry from 8.270 to 10.640 and conductivity from 1.24 to 3.79 mS/cm). This process avoids the isoelectric point at pH around 8 – 9. When the slurry was well mixed (pH, conductivity and temperature reaching stability), it was pumped through the milling chamber, UAS and DLS, and then back to the mixing tank. Then, the measurement sequences were taken at every 3 min. The pump speed was set at 1200 rpm to prevent particle sedimentation in the UAS measurement cell. Pump speed set initially at 650 rpm yielded poor quality of attenuation spectra, evidently caused by sedimentation of particles in the UAS measurement cell. Higher pump speed was tested and proved to be capable of avoiding sedimentation.

IV. RESULTS AND DISCUSSIONS

A. *Spectral data*

The coupled-phase model [6] was used to generate the ultrasonic attenuation spectra for establishing the MSPC model. Six hundred ultrasonic attenuation spectra were generated by randomly inputting the required product specifications in the ranges of median size [90 – 200] nm, standard deviation [0.1 – 0.5] nm and concentration [1 – 5] vol.% into the coupled-phase model, to obtain the attenuation spectra. These spectra were treated by PCA following Eqs. (2) - (4). The analysis showed that two principal components ($k = 2$) were adequate to describe the generated spectra, in as much as they captured approximately 99.9% of the variance. Hence in MSPC model development, two principal components are used.

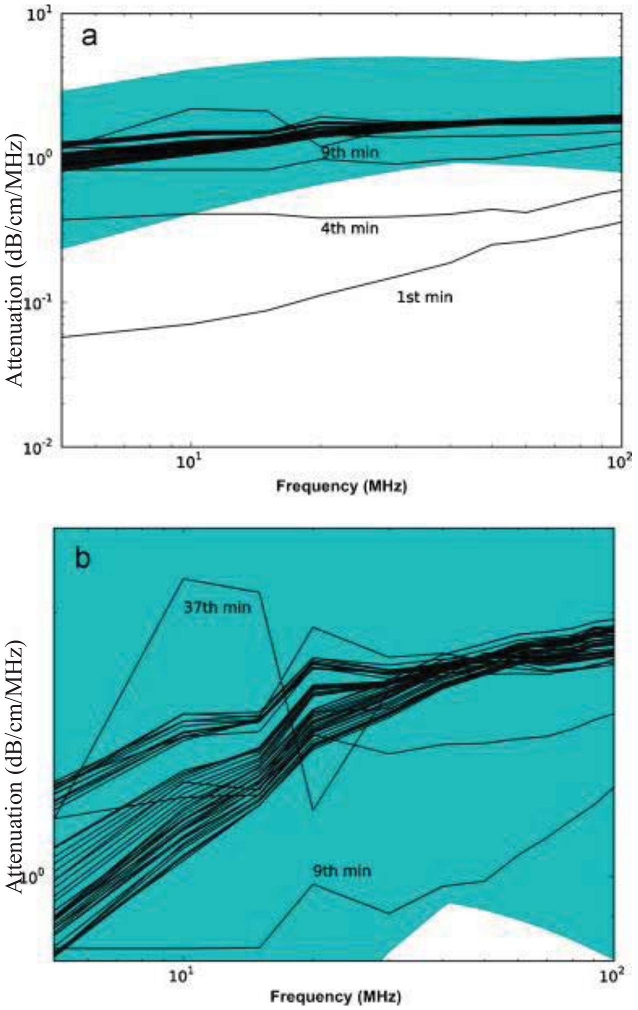

Figure 2. Measured ultrasonic attenuation spectra.

B. Hotelling's T^2 and SPE charts

The obtained attenuation spectra from the milling experiment were further analysed to obtain their scores, by projecting onto two new variables.

The obtained measured attenuation spectra have been analysed for establishing monitoring charts following Eqs (2) - (4) and the Hotelling's T^2 and SPE charts are shown in Fig. 3 and Fig. 4, respectively.

The Hotelling's T^2 chart in Fig. 3 represents the moving of the spectra via the scores during the milling time. At the first minute, the T^2 is out of the upper control limit. This is an indication that the particle median size may not be able to meet the specification. With increasing the milling time, the T^2 decreases and moves close to the required specification. Until the milling time reached the 9th minute, the T^2 indicates that it is in-specification which can be seen in Fig. 3 that the T^2 is lower than the upper confidence limit. This can be confirmed by the characterisation of the milled alumina as shown in Fig. 5 that at the time 9th minute the particle median size was 178 nm. In addition, when the milling time was increased, the particle median size was nearly stable. The final size was 116 nm which is within specification.

The square prediction error (SPE) chart in Fig. 4 aims at detecting abnormal events which is not included in the NOC data. The figure shows that only one point is out of the upper confidence line, at the accumulating time 37th minute. When examining the attenuation spectrum (see Fig. 2) at that time, it can be seen that the quality of the spectrum was not good (not smooth curve).

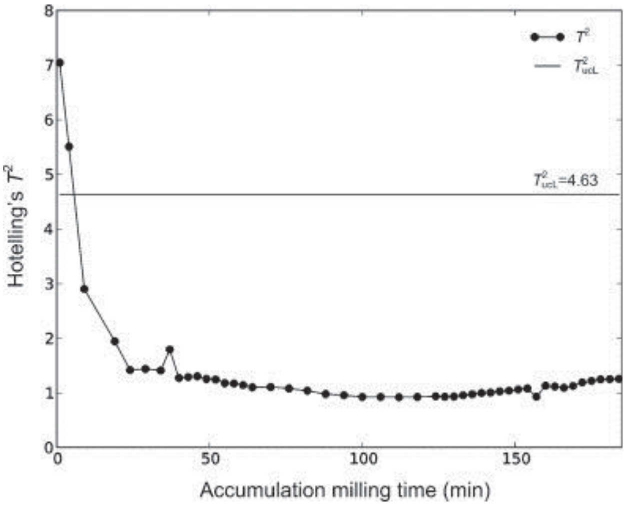

Figure 3. Hotelling's T^2 of the measured spectra.

C. Advantage and limitation of MSPC

MSPC monitoring uses both Hotelling's T^2 and SPE charts. The Hotelling's T^2 chart (Fig. 3) monitors the probability that the operation is within normal operation, based on the normal operation data used for training. If a totally new event occurs which was not seen in the training data, SPE (Fig. 4) chart should be used. Since the current MSPC model is created using NOC data based on the coupled-phase model with the specific input and material properties, it is not applicable to other systems such as silica or other size ranges. This is a limitation of the method.

In addition, the current model was built based on the NOC spectra generated from an instrument process models, the coupled-phase model at relatively low solid concentrations. This has been done mainly for the purpose of demonstrating the idea. In real applications, NOC data should be collected from the real process.

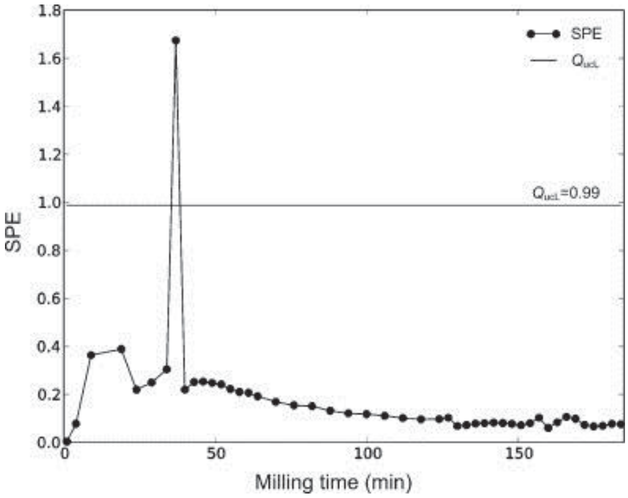

Figure 4. Square prediction error of the measured spectra.

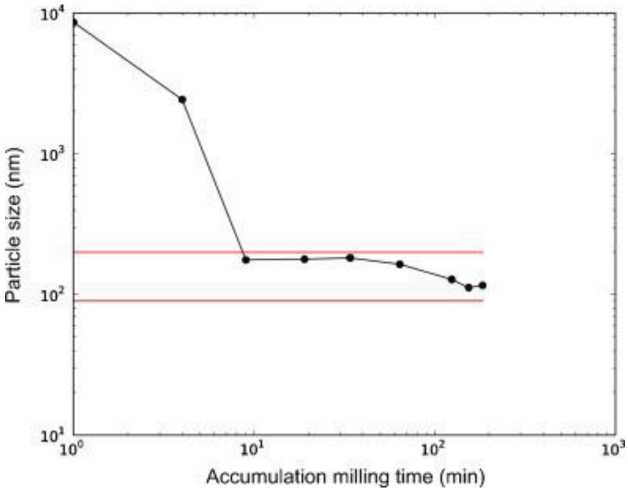

Figure 5. Particle median size of the experiment.

V. CONCLUSIONS

A major challenge of applying ultrasonic attenuation spectroscopy (UAS) to on-line process monitoring and control has been due to the fact that existing instrument process models cannot take full consideration of particle – particle interaction and multiple scattering. The proposed method of making use of the raw UAS spectra for multivariate statistical process control (MSPC) using Hotelling's T^2 and square prediction error (SPE) provides a potentially useful approach for process and product quality control in nanomaterial processing. Although the normal operational data was created using a coupled-phase model, it nevertheless demonstrated the idea using the batch wet nanomilling process.

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