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# A 2D autocorrelation method for assessing mixture homogeneity as applied to bipolar plates in fuel cell technology

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## A B S T R A C T

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Scale of segregation  
Bipolar plate  
Fuel cell technology  
Moran's index

This paper presents a methodology based on spatial autocorrelation function for assessing homogeneity of a mixture and more particularly for determining the size and the number of defects in the bulk of a mixture or materials. Intensity and scale of segregation are used as conceptual tools for assessing mixture homogeneity, and have been specially adapted for this particular case. Their performances are investigated for detecting defects in a product manufactured from a dry powder mixture, a bipolar plate used in fuel cell technology, through a simulation of the product on Matlab (92).

## 1. Introduction

Assessing mixture homogeneity is a key issue in many industries involved in solids processing. The general heterogeneity of a mixture is known to have an influence on the taste of a food product or the bioavailability of a drug. Several criteria based on the variance of composition of samples have been derived to access to a macroscopic quality standard which is used in the industry to accept or reject a mixture. This also results in dramatic costs increase, especially in the pharmaceutical industry in which recycling is not allowed. But even if this global criteria is satisfied, the presence of punctual defects in the mixture can drive to a lack of processability and to a loss of quality of the final product. Such a "hot point" can affect dramatically the mechanical resistance of a piece of material made of concrete, or change the visual appreciation of a food product. This is also the case in the field of bipolar plate manufacturing, in which mechanical, electrical and thermal characteristics of the plates are key properties to guarantee.

Fuel cells convert chemical energy into "clean" electrical energy from hydrogen and oxygen, the only wasted product being clean water. They consist in a stack of individual cells (Fig. 1). Bipolar plates interconnect individual cells and provide connections to the outside. Their roles are to conduct electricity, keep the reaction gases separated, and channel away waste water and heat from the reaction. However, the widespread adoption of fuel cells is limited by the cost of key components as bipolar plates. The manufacture

of efficient, reliable and low cost bipolar plates is now a crucial economic issue to allow implementation of fuel cells in industrial and domestic applications. Bipolar plates may be prepared by thermosetting of dry powder mixtures consisting of graphite, epoxy resin, as well as some minor additives. The formation of polymer aggregates is sometimes observed during the mixing step. These aggregates are known to lead to mechanical deficiencies of the plates, which may cause their rupture during the demolding step. Determination of the size and number of polymer aggregates in a plate could therefore help to define better criteria for their acceptability.

In a first approach, it might seem indicated to link the detection of defects on the surface of a materials or a mixture to image analysis. However, defects can be located in the bulk material, mixture or plate and may therefore not be visible, making image analysis of disputable use. The purpose of this work is to develop a methodology which can be applied regardless of the analytical method used in the measurement of sample's composition. We will focus on the methodological tools developed to study powder mixture homogeneity and then we will present an extension aiming at detecting defects in a bipolar plate.

## 2. Mixture homogeneity

The first definition for assessing homogeneity of mixtures was introduced by Danckwerts in 1952 [1]. He suggested the use of two concepts: the intensity and the scale of segregation. The first

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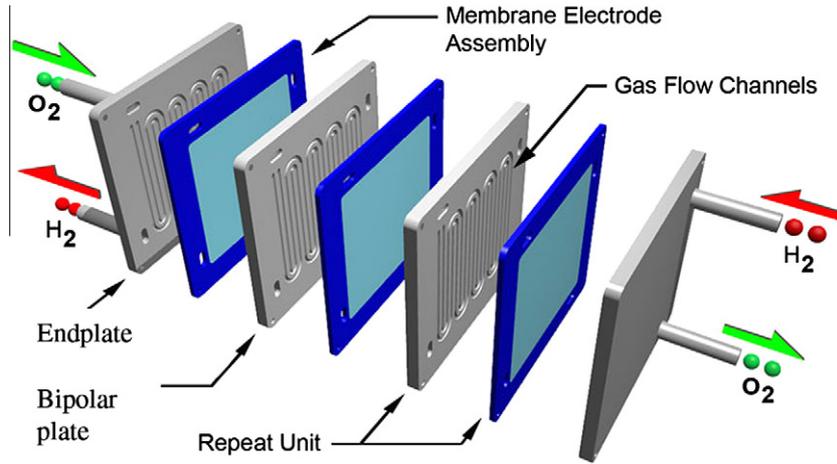


Fig. 1. Schematic representation of a fuel cell stack [17].

one studies fluctuations among sample's compositions, while the second one describes the state of subdivision of clusters.

Let us consider a mixture made of two components (A and B) being divided into  $N$  samples of a certain size. Let  $\bar{a}$  and  $\bar{b}$  be the mean composition of the mixture in component A and B, respectively, and  $\sigma_a$  and  $\sigma_b$  the corresponding standard deviations. In Danckwert's definition, the intensity of segregation is calculated as:

$$I = \frac{\sigma_a^2}{\bar{a}\bar{b}} = \frac{\sigma_b^2}{\bar{a}\bar{b}} \quad (1)$$

A decrease of segregation intensity reflects the fact that the composition of each sample is close to the mean composition of the mixture. Instead of the definition proposed by Danckwerts, it is usual to consider the coefficient of variation, which varies in the same way as the variance but may be less dependent on the mean. CV could be used for a mixture of more than two components. Let us consider a mixture cutted into  $N$  samples, for which a key component has been defined. Let  $x_i$  be the composition in key component in sample  $i$  and  $\bar{x}$  the mean composition in the samples. The CV of the mixture over the  $N$  samples reads:

$$CV = \frac{\sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2}}{\bar{x}} \quad (2)$$

Indexes have been developed, based on the comparison of the standard deviation of the mixture with those of limit cases (random mixture, totally segregated mixture) but none allows to reach a better definition of the mixing homogeneity. Poux et al. [2] made a summary of the different indexes and Fan and Wang [3] reported a comparison between some indexes.

The intensity of segregation qualifies the state of macromixing [4]. It gives no information about the structure of a mixture. In Fig. 2, four different mixtures are represented. Each of them has the same CV but their structures are completely different. It may

happen that they could also drive to different end-used properties. To describe this, Danckwert suggested the use of a second concept, the scale of segregation. This tool provides information about the shape and the size of agglomerated particles and could therefore be linked to the size of defects.

The autocorrelation function,  $R(r)$ , among composition  $x_i$  of  $N$  consecutive samples, is applied to determine its numerical value by analogy to the scale of turbulence used in the statistical theory of turbulence.

$$R(r) = \frac{\sum_{i=1}^{N-r} (x_i - \bar{x})(x_{i+r} - \bar{x})}{\sum_{i=1}^N (x_i - \bar{x})^2} \quad (3)$$

$r$  is the distance between two samples

In the associated autocorrelagram (see Fig. 3),  $\varepsilon$  corresponds to the limit beyond which  $R(r)$  may be considered to be equal to zero, being  $r_0$  the corresponding value of  $r$ . This results from statistical thoughts [5] and depends on the confidence interval. For example, if a confidence interval of 95% is considered, then:

$$\varepsilon = \frac{2}{\sqrt{N}} \quad (4)$$

$R(r)$  always lies between  $-1$  and  $+1$ . A high value of  $R(r)$  means a strong correlation between samples compositions separated by a "distance" equal to  $r$ . Therefore  $r_0$ , also called the specific lag, corresponds to the number of samples that are correlated among each other [5]. Danckwerts defined the scale of segregation,  $S$ , as the area under the curve:

$$S = \int_0^{r_0} R(r) \cdot dr \quad (5)$$

$S$  can be approximated by the trapezoidal method. However the determination of the autocorrelation function follows a discrete way and consequently the number of points may be too small to

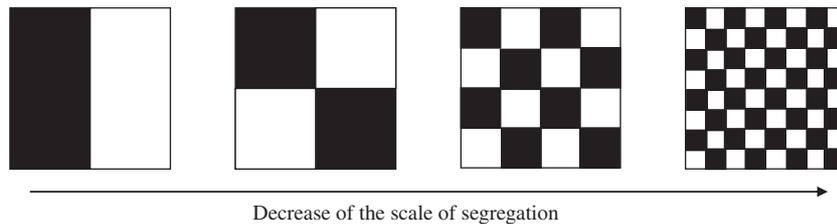


Fig. 2. Representation of the scale of the segregation according to Schofield [6].

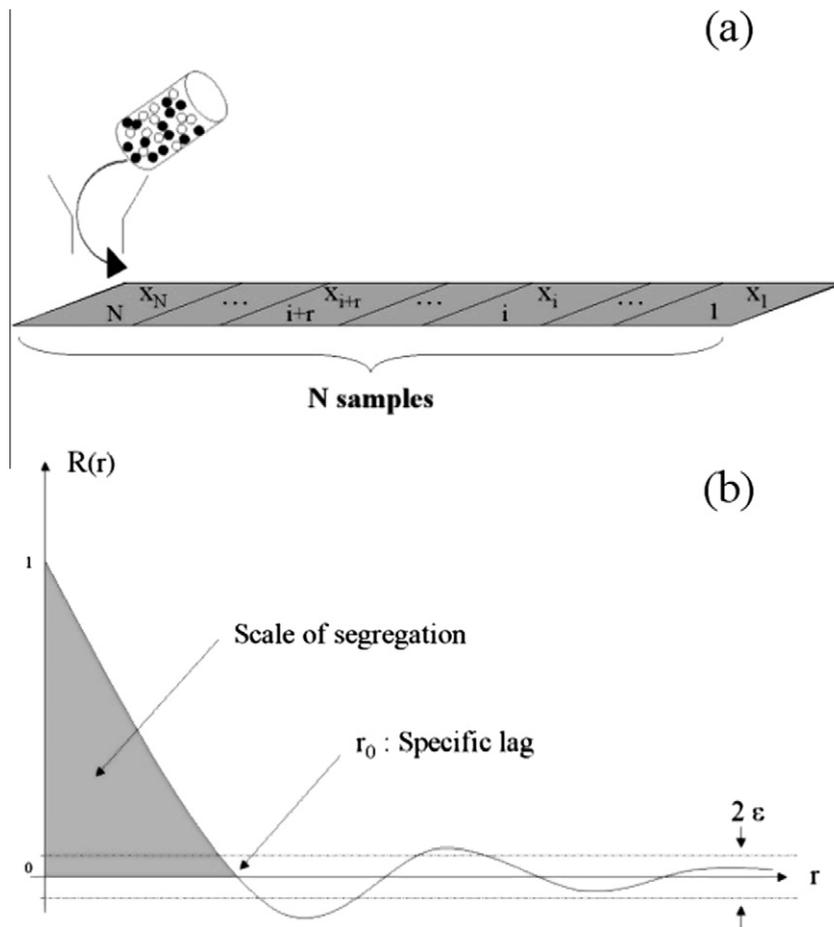


Fig. 3. Discharge of a mixer onto a conveyor and cutting the mixture into  $n$  samples (a) as in Massol-Chaudeur et al. [4]. Representation of the related autocorrelogram (b).

apply this method. The values associated may lead to some major errors in calculations. This makes  $r_0$  most likely used instead of  $S$ , because its determination is easier and more precise.

Although the scale of segregation provides interesting information on the mixture's structure, examples of its use in assessing powder mixture homogeneity are scarce. We can mention the work by Schofield [6] and, more recently, the one by Gyenis [7]. Both have linked the scale of segregation to the mixing mechanisms and particularly to convection through some simulations. Schofield has shown that autocorrelograms give rise to suitable indexes of mixedness for predominantly convective mixing mechanism. When diffusion becomes the limiting phenomena, the autocorrelation data are more difficult to interpret. Gyenis conclusions followed the same way. He proved that the correlation technique assesses the degree of homogeneity and reveal the microstructure of concentration pattern, especially at the early stages of the process (i.e., convective and shear mechanism).

Very few other papers have been published on the subject. As a matter of fact, the determination of the scale of segregation (or the  $r_0$  associated) requires exhaustive sampling ideally at different scale of scrutiny. The collection of accurate data is somewhat a tedious task and authors [8,9] concluded that this measure is difficult to be performed for a real case, so that such a tool could not be used as a chore. However, with on-line analytical techniques, the study of a larger number of samples in a short time looks now possible. Autocorrelation could therefore appear now as a viable tool for a better understanding of mixing process and mixture structure.

Danckwert's approach is based on time series models where only one direction is used (the future is only determined by the

past and the present). Thus, the determination of autocorrelation coefficients can be done only for long thin (row) samples. For a better determination of scale of segregation in space ( $I$ - $e$  cluster shape and size) a 2D approach is needed. Schofield [6] extend this theory to a 2D and 3D approach of the mixture by averaging at a lag  $r$ , for each value of  $i$ , the different product  $(x_i - \bar{x})(x_{i+r} - \bar{x})$  obtained in the three directions. In the same way, but in a different field, it was used for studying the microstructure of a 3D porous media [10,11]. It seems that a spatial approach could gain accuracy in the determination of the scale of segregation and the understanding of mixing mechanism. Closely related problems also arise in geographical or economics and some of this extensive work is summarised by Cliff and Ord [12].

### 3. Spatial autocorrelation

Spatial autocorrelation studies the correlation of a variable with itself through space. Thus if there is any systematic pattern in the spatial distribution of sample's composition, it is said to be spatially autocorrelated. If nearby or neighbouring areas have composition more alike, this indicates positive spatial autocorrelation. On the contrary, negative autocorrelation describes patterns in which neighbouring areas are unlike. At last, random patterns exhibit no spatial autocorrelation.

Several spatial autocorrelation indexes have been proposed. The most known and used follows Moran's and Geary's statistics [12]. Each index gives a specific information. Moran's coefficients compare the value of a composition at a definite location with the values at all other locations. Formally, it is defined as:

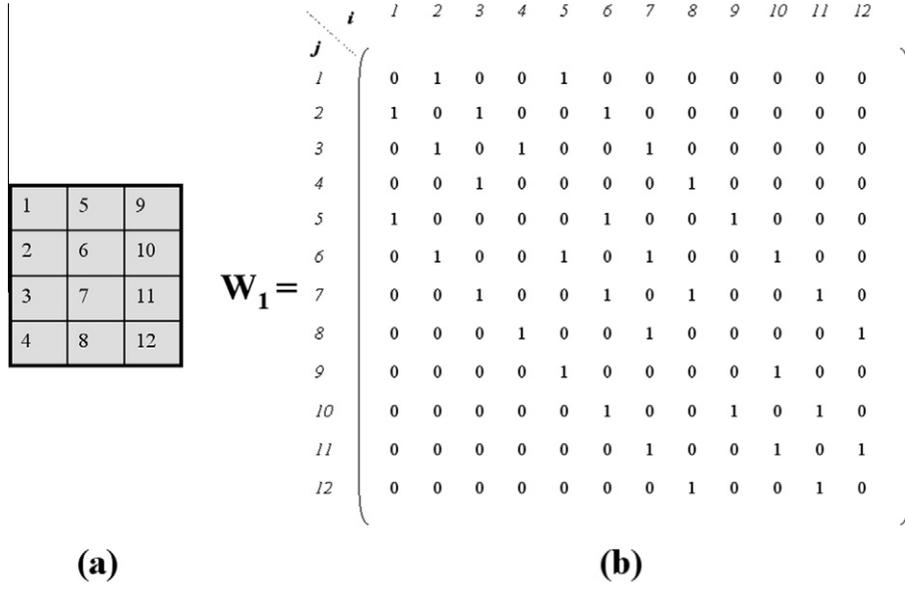


Fig. 4. Neighbouring matrix (b) for a plate (a) cut in 12 samples at the lag  $r = 1$ .

$$I(r) = \frac{N * \sum_i \sum_j W_r(i,j) * (x_i - \bar{x})(x_j - \bar{x})}{S_0(r) * \sum_i (x_i - \bar{x})^2} \quad (6)$$

$$S_0(r) = \sum_i \sum_j W_r(i,j) \quad (7)$$

Geary's coefficients are similar to Moran's. However the interaction is not the cross-product of the deviation from the mean but the deviation in intensities of each sample composition with one another. It is defined as:

$$C(r) = \left( \frac{N-1}{2 * S_0(r)} \right) * \frac{\sum_i \sum_j W_r(i,j) * (x_i - x_j)^2}{\sum_j (x_j - \bar{x})^2} \quad (8)$$

As a consequence, Moran's coefficients give a more global indicator whereas Geary's coefficients are more sensitive to differences in small neighbourhoods [13].  $I(r)$  varies in the same direction as Danckwert's definition (between  $-1$  and  $1$ ).

In both definitions, the spatial dimension is introduced thanks to  $W_r(i,j)$  called contiguity or neighbouring matrices. It indicates the proximity of two samples at the lag  $r$ .  $W_r(i,j)$  equals 1, if sample  $i$  is neighbouring sample  $j$  to the distance  $r$  (Fig. 4). In the simplest case, two samples are neighbouring if  $r$  borders must be crossed to join them. A border is defined as a line between two samples. This means that contact points are excluded. Another option is to make  $W_r(i,j)$  a distance-based weight which is the inverse distance between locations  $i$  and  $j$  ( $1/d_{ij}$ ). In this case  $W_r(i,j)$  are called weight matrices.

#### 4. Methods and simulation

The methodology we suggest for studying the number and size of defects inside a bulk mixture, or a finite product like a bipolar plate, is based on the coefficient of variation and Moran's Index (using for  $W_r(i,j)$  a neighbouring matrixes). This may help in staying closer to Danckwert's definition of the intensity and the scale of segregation.

First, the materials studied are virtually cut into  $N$  parallelepiped rectangles samples according to two directions. Neighbouring matrices  $W_r$ , at different lag  $r$ , are built.  $W_r$  will be a  $N * N$  matrix

with each diagonal element equal to zero as a sample cannot be neighboured by himself. Then the coefficient of variation CV and the Moran's coefficient are calculated. The autocorrelogram associated to Moran's coefficients is represented graphically and the specific lag  $r_0$ , such as  $I(r_0) = 0$  is determined. A value of  $r_0$  lesser than 1 indicates that there is no correlation among samples.

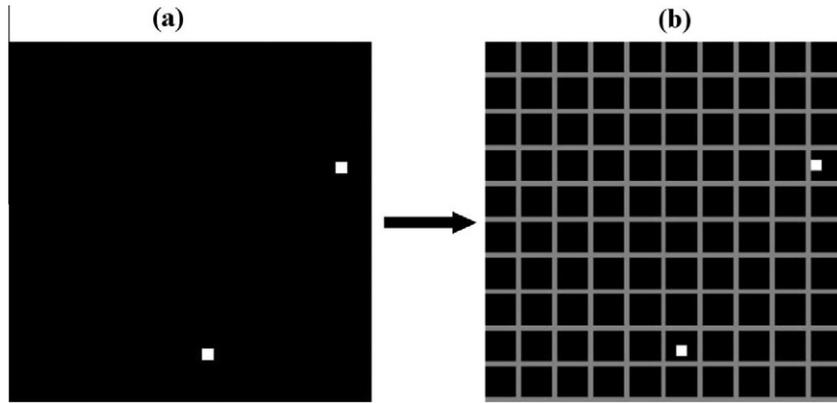
We study here a simulated typical bipolar plate manufactured from thermoset polymer and graphite. Let us consider its dimensions as being  $60 \text{ cm} \times 60 \text{ cm} \times 0.5 \text{ mm}$ . It can be regarded as a two dimensional array of parallelepiped rectangles called unit samples. Unit sample size should be related to the smallest scale of scrutiny that is considered. In this study, dimensions for unit samples were set at  $1 \text{ mm} \times 1 \text{ mm}$  and  $0.5 \text{ mm}$  for the thickness (total thickness). The bipolar plate is therefore represented by a  $60 * 60$  matrix. Each element of the matrix takes the value of the composition in the key component (graphite) in the unit sample considered.

Simulation of bipolar plate composition was realised in Matlab. The plate studied had the following composition: 15% for thermoset polymer and 85% for graphite. This composition corresponds to a real case of manufactured bipolar plate which allows to meet the requirements for thermal and electrical conductivity and mechanical strength of the bipolar plate. Defects were assigned to the plate with a composition in thermoset polymer equal to 100%. Number and size of defects were studied. Their locations were determined randomly. We assumed a perfect mixing state all around defects (Fig. 5a). The bipolar plate is then divided into cubic regions or samples (Fig. 5b) whose compositions are stored in a matrix. The coefficient of variation and the autocorrelation coefficients according to Moran's model were calculated. The specific lag  $r_0$  has been determined as follows: if  $y(r)$  is a linear regression between the last value upper and the first value below the error bar, the number of correlated samples,  $r_0$ , would be determined from  $y(r_0) = 0$ .

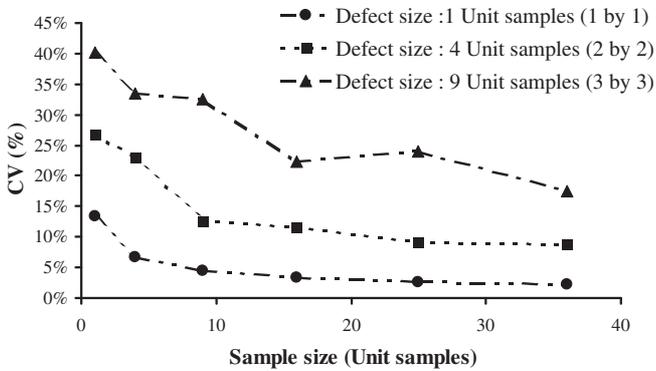
#### 5. Results and discussion

##### 5.1. Influence of the sample size

The importance of the scale of scrutiny has been discussed in numerous articles [14–16]. The scale of scrutiny (i.e., the "best" sample size) must be defined as the final product meets the



**Fig. 5.** Representation of a bipolar plate obtained from Matlab simulation with 2 defects (defect size: 2 by 2 unit samples). In black: homogenized mixture; in white: thermoset polymer defects (a). Cutting of the plate (a) in 100 samples (sample size 6 by 6 unit samples) (b).

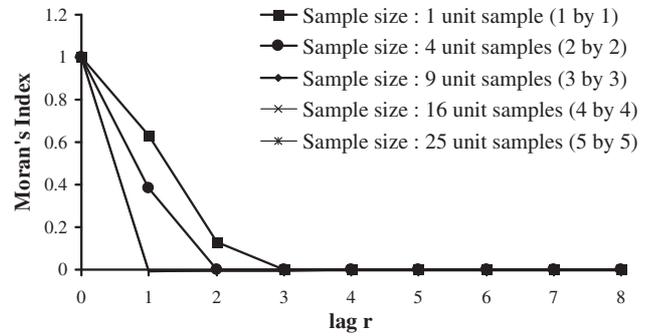


**Fig. 6.** Evolution of the coefficient of variation with sample size.

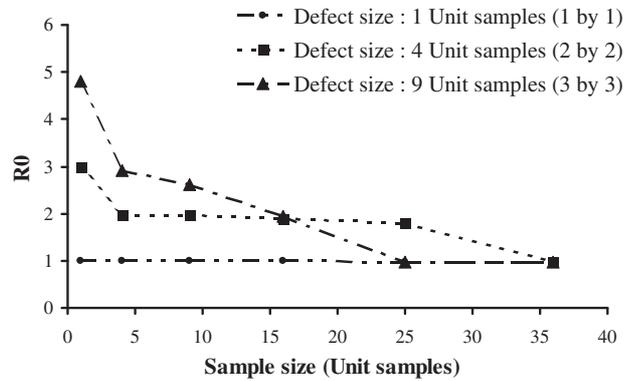
specifications it is intended for. Take the example of a powder mixture used to produce pharmaceutical tablets: the scale of scrutiny makes sense, it must be equal to the size of a tablet. In other field or applications, it can be more difficult to define. For a bipolar plate, specifications are of electrical, chemical, thermal and mechanical orders which makes scale of scrutiny not easy to define. Regions (samples) of different sizes were therefore considered to study its influence on the coefficient of variation and the specific lag. Hereafter, cubic samples from 1 (1 by 1) to 36 (6 by 6) unit samples were considered.

Consider two bipolar plates, each containing two defects of identical size. For the first one, the defect size is set to 2 by 2 unit samples, and for the second one, the defects size is set to 3 by 3 unit samples. Fig. 6 shows the evolution of CV versus sample size. It appears that increasing the sample size implies a reduction of variance. It may be noted that this variation is not linear. When the sample size (i.e., scale of scrutiny) is greater than the defect size, we observe very few changes in CV value. In fact, the CV allows to see imperfections in a mixture (or a material) whose sizes are greater than the scale of scrutiny. This means that a defect of a size smaller than that of a sample cannot be seen.

Spatial autocorrelation coefficients were calculated following Moran's definition (Fig. 7).  $r_0$  decreases with increasing sample size up to 1 (Fig. 8). However, the curve obtained for a defect size of 9 unit samples reach 1 faster than the curve obtained for a defect size of 4 unit samples. To explain this phenomenon, let's have a look at the two bipolar plates that correspond to curves previously mentioned and to their cutting into samples size of 25 unit samples (5 by 5) (Fig. 9a and b).



**Fig. 7.** Moran's index obtained for a bipolar plate of defects (defect size: 2 by 2 unit samples). Different sample sizes have been considered.



**Fig. 8.** Evolution of the specific lag  $r_0$  with increasing sample size.

In this example, a defect of the size of 4 unit samples (2 by 2) is cut in two samples causing a higher  $r_0$ , while defects with a larger size (9 unit samples: 3 by 3) are each included within a single sample causing a  $r_0$  value less than 1. Thus, when the defect size is lower than that of the sample, the cutting has a strong influence on the value of  $r_0$ . To investigate the influence of the defect's size and their number on CV and  $r_0$ , only sample sizes greater than those of the defects have been considered.

### 5.2. Influence of the defect size and the number of defects

Evolution of CV and specific lag  $r_0$  have been studied for a bipolar plate with 2 defects of different sizes (Fig. 10). Sample size is set

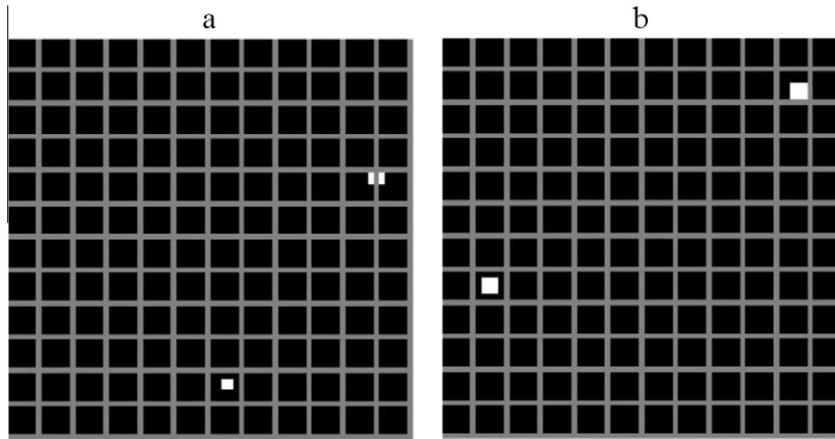


Fig. 9. Bipolar plate with two defects of size 2 by 2 unit samples (a) and two defects of size 3 by 3 unit samples (b). Cutting into samples of size 5 by 5 is shown (grey lines).

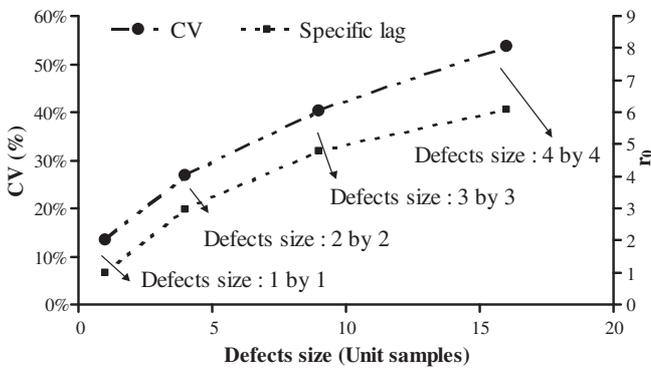


Fig. 10. Profile of CV and  $r_0$  with increasing defects size.

to 1 unit sample. An increase of the defects size involves an increase of CV and specific lag. It is interesting to note that slopes seem almost parallel. This highlights the fact that an increasing defects size has the same impact on CV and specific lag.

For a defect size set, when the number of defects increases, the CV also increases (Fig. 11a). Conversely, the variation of  $r_0$  seems to be low (Fig. 11b). However a systematic small decrease of  $r_0$  is observed with the number of defects. We think that it could be linked to the fact that if the number of defects increases, they could be considered as an integral part of the plate rather than singular occurrences.

To sum up, number of defects have an influence only on CV while defects size affects both CV and specific lag. Thus defects size seems rather linked to the specific lag. Once the defect size is estimated, the CV could provide indications about the number of defects.

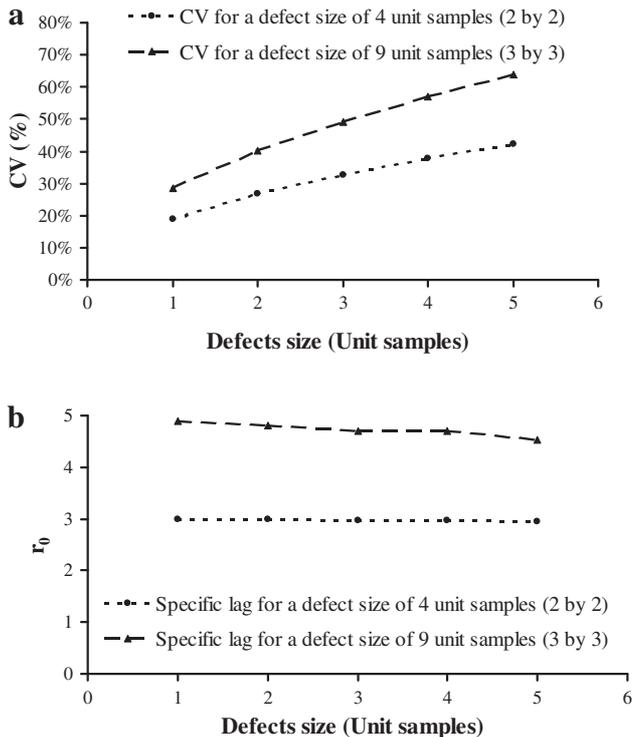


Fig. 11. Evolution of CV (a) and specific lag (b) with increasing defects size.

## 6. Concluding remarks

In this paper, we have developed a methodology for analyzing defects in 2D. This methodology allows the detection of defects in the bulk of a mixture or materials, only from samples compositions. It has been applied to a bipolar plate through a simulation of defects on the plate. As expected, an increase of sample size (scale of scrutiny) led to a decrease of the CV and the specific lag until the sample size is greater than those of defects. Otherwise the cutting into samples has a great influence on the value of  $r_0$ . It has been highlighted that an increase in the size of the defects implies an increase of the CV and  $r_0$  and both follow the same profile increase. It has also been demonstrated that if an increase of the number of defects involves an increase of the CV,  $r_0$  remains almost constant and is more likely related to the size of the defect. Indeed, a knowledge of these two parameters could enable the identification of defects giving ideas of their numbers and their sizes. Future work will focus on investigating the effect of a non perfect mixture around the defects and the influence of the presence of defects of different sizes in the same plate.

## Acknowledgements

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