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1. Description of task 2.11

The objective of D.2.11 is to review and validate measurement methods for volume specific surface area (VSSA) with the aim of proposing a simple, reliable, cost-effective methodology. Finally, define a Protocol(s) for VSSA analysis of primary MNM objects in the air, powders, and liquids in compliance with the EU definition.

As per the EU recommendation, the VSSA of 60 m²/cm³ was established assuming ideal mono-modal size-distributions and with known skeletal densities. Considering the nanomaterials definition, if 50% of the nano-objects by number are between 1 and 100 nm along their shortest dimension, the VSSA criterion becomes less apparent. However, for potential implementation of the VSSA criteria, it is necessary to understand the potential influence of morphology, size distributions, surface or internal organic coatings, etc.

To implement a straightforward and effective way of assessing the "nano" character powder samples, wherein we intend to develop a protocol for measuring VSSA. To correctly estimate VSSA, a close cooperation were established with the teams determining the particle size distribution by electron microscopy technique (Tasks 2.2.a and 2.3.b).

2. Description of work & main achievements

2.1. Summary

The theoretical and experimental work carried out during the project demonstrated the applicability and the reliability of the VSSA approach to identify nanomaterials in powders for mono-modal particle size distributions. Both nitrogen sorption isotherms and particle size measurements by TEM were used to validate the applicability of the VSSA approach.

The VSSA approach is reliable to identify nanomaterial under the following conditions:

The adsorption data should be of good quality (effective degassing of the sample, equilibrium at each experimental point, sufficient number of experimental points to cover the relative pressure range from 0 up to 0.65). If these conditions are respected, then the analysis of adsorption isotherms via the BET and the t-plot transformations will give reliable results.

It is necessary to have an elementary knowledge of the material under test like its chemical nature, the presence of a coating and some structural data. In particular, a qualitative image by transmission electron microscopy is needed to define the particle shape. It is recommended to use skeletal density for calculation of VSSA.

It is suggested to follow the process described hereafter

If the VSSA is lower than the threshold (i.e. 60 m²/cm³ for spherical particles), then the sample should be considered as non-nanomaterial.

If the VSSA is higher than the threshold (i.e. 60 m²/cm³ for spherical particles), then the t-plot should be used to detect the presence of an internal porosity or the presence of a coating and to estimate the external surface of the particles as illustrated several times in this report. This external surface is then used to calculate

the VSSA which is compared to the threshold to decide if the sample is nano- or non-nano- according to the EU definition.

Applying this procedure to several types of samples, it appears that all the test samples were correctly identified by this VSSA approach. However, as predicted by the modelling, the VSSA approach may be overprotective, leading to the false identification of nanomaterials.

As a consequence:

- If the VSSA is lower than the threshold, then the material may be considered as a non-nanomaterial.
- If the VSSA appears to be slightly higher (up to about 20%) than the threshold, it is necessary to determine the particle size distribution by TEM image analysis to decide whether the material is a nanomaterial or not.
- If the VSSA is much higher than the threshold, the material should be considered as a nanomaterial.

This confirms that the VSSA criterion is a simple, practical way to assess the “non-nano” character of a material without using expensive advanced methods based on number particle size distribution, such as TEM. The outcome of this task, protocol D2.11 (Annex 1), intends to provide insights on how to demonstrate the potential of using adsorption isotherms to describe the texture of nanomaterials and hence to be able to determine the VSSA value either by the BET or the t-plot transformation. This conclusion is comforted by the results of the theoretical study.

2.2. Background of the task

The VSSA concept was introduced to characterize the size of a monodispersed distribution of spherical, non-porous particles. Such an ideal model simply uses the ratio surface/volume of the particle, which is easily understandable when all the particles are spherical and have the same size. However, in reality, the nanoparticles have a high tendency to aggregate or agglomerate, and hence the VSSA should consider the reality of the nanomaterials. In practice, it is important to assess how the VSSA concept can be applied to polydisperse distributions of non-spherical particles.

A theoretical approach was developed to determine the role of particle shape and polydispersity on the VSSA concept and a model to calculate VSSA for polydisperse non-spherical particles was proposed. To avoid confusion, the VSSA obtained by this model is called total VSSA. These calculated values will then be compared to the measured ones.

The most feasible approach to determine the VSSA is by combining the BET surface area and the skeletal density of the powder. The BET surface area analysis normally, include both the external and internal surface (porosity) of the particles while the VSSA concept for identification of an MN may be linked to the external dimensions of the particles. If the particles have an internal porosity (i.e., the porosity from micropores, micro channels, cracks in particles,..., etc.), the BET surface area will be larger than the external surface area and will result in an identification of false positive nano-materials. It means that numerous powders can potentially be falsely identified to consist of MN.

A methodology to complete characterisation of powders by in-depth analysis of nitrogen adsorption isotherms was demonstrated to enable the discriminate between the external and internal surface areas in powders. The method is readily applicable

to the dry powders without any treatment. For the solid suspended in liquid like colloids, the suspension could potentially be gently dried to collect the solid part.

The objective of this study is to determine the applicability and reliability of the VSSA approach to distinguish between nano- and non-nano-materials without necessarily using the number particle size distribution.

The work was carried out in the following stages:

- As a first step, a theoretical study of the effect of particle shape and particle size distribution on the VSSA values and thresholds has been carried out and a model to calculate the VSSA from the number particle size distribution was developed taking into account the particle shape.
- As a second step, a draft protocol of measurement based on an in-depth analysis of the nitrogen adsorption isotherm was elaborated based on the existing expertise and ISO and IUPAC recommendation.
- In a third step, several samples have been identified and collected to test the draft protocol by three different laboratories, to assess the repeatability and the reproducibility of the results and to amend the draft protocol accordingly.
- The particle size distributions obtained by electron microscopy on the provided by the task 2.10, were used to calculate the corresponding VSSA values by the model developed in the first step. These VSSA values were compared to the VSSA values obtained by analysis of the nitrogen adsorption isotherms.
- Finally, the protocol was amended and the second series of samples (nano and non-nano) were studied both by adsorption and electron microscopy to confirm the applicability of the VSSA approach to identify nanomaterials.

2.3. Description of the work carried out

2.3.1 Theoretical approach

A theoretical study was carried out to identify the effect of the particle shape, polydispersity, agglomeration and aggregation on the VSSA threshold. The key results are summarized hereafter.

2.3.1.1 Effect of particle shape

The proposed VSSA threshold $60\text{m}^2/\text{cm}^3$ is calculated for a monodispersed distribution of spherical particles with a 100 nm diameter. A generalization of the use of VSSA to another non-spherical particle can be considered by defining a characteristic, representative dimension corresponding to the smallest size of the particles.

The concept of an “equivalent sphere diameter” is typically dependent on the measurement technique and may not apply to decide if a material is a nanomaterial or not. It is better to define a characteristic size for each particle shape. Such an approach was made for various particle shapes considering for particles of unit density; the VSSA is simply the ratio between the external surface area of the particle and its volume. As a result of this study, it appears that the VSSA threshold value varies from $60\text{m}^2/\text{cm}^3$ for spherical or cubic particles to $40\text{m}^2/\text{cm}^3$ for fibers and rods; to $20\text{m}^2/\text{cm}^3$ for sheet-like or platelets objects. Intermediate values can be considered if the aspect ratios for rods or platelets is known.

Depending on the particle shape and characteristic size, the VSSA threshold value for monodispersed particle size distribution, can be expressed by:

$$\text{VSSA} = a/D,$$

where D represents the characteristic size of the particle and “ a ” is a positive numerical constant depending on the shape and on the density of the particles.

2.3.1.2 Effect of porosity

The use of VSSA concept as a criterion to measure the particle size implies that the particles are non-porous. If it is not the case, only the external surface area of the particles may be used. Nitrogen sorption isotherms and BET surface area have been used to assess the surface of the powder particles. The BET surface area often includes an internal porosity of the primary particles, and this approach may result in a false identification of nanomaterials. It means that a lot of materials will be falsely considered as “nanomaterials” in particular if the particle has an internal nano-porosity (zeolite for example) or a porosity generated by an inorganic coating (like in coated titanium oxide pigments).

Hence, one of the objectives of this report was also to develop a methodology to discriminate the external and the internal surface area of the particles (including the presence of a coating) by analysis of nitrogen adsorption isotherms. Refer to Chapter 2.3.2 for further details on this topic.

2.3.1.3 Effect of polydispersity

According to the EU definition, to identify nanomaterials, particle size distribution based on the number concentration is proposed. Transmission electron microscopy (TEM) is primarily used to determine such a distribution, but it requires more reliability on counting a large number of particles for example with poly-modal or broad size-distribution. Therefore, use of VSSA as a screening method for known materials would be of benefit.

- **Mono-modal particle size distribution**

If the particle-number-size distribution is known, it is possible to calculate the diameter or the smallest characteristic size of the particles (i.e. diameter of fibers or thickness of platelets) corresponding to the 50% number concentration when the distribution is of the normal or lognormal type. For a normal distribution characterized by the parameters (the median μ and the variance σ^2), the 50% number concentration corresponds to the median μ expressed in nm.

For a lognormal distribution, characterized by the parameters μ and σ^2 , the 50% number concentration corresponds to the median “ $\exp(\mu)$ ” where μ is expressed in nm. For any other type of distribution, the 50% number concentration corresponds to the median that can be calculated from experimental data by using an appropriate statistical program.

If the median of the distribution based on the number concentration corresponds to a characteristic size less than or equal to 100 nm, then the sample is considered as a nanomaterial according to the EU definition.

If the median of the distribution is larger than 100 nm, and less than 50% of the particles are in the 1-100 nm range, consequently, the sample is not a nanomaterial according to the EU definition. The question is: “how would the VSSA concept, apply to polydisperse non-spherical particle size distributions?” In other words will the criterion based on the number particle size distribution and the criterion based on the VSSA concept be compatible to identify nano-materials? It is interesting to link both

approaches by developing models to calculate VSSA starting from the particle size distribution. This theoretical modelling approach is presented hereafter.

As a result of the discussion on the effect of the particle shape, it is indeed possible to consider that the VSSA value, for a mono-dispersed particle size distribution, can be, whatever its shape, expressed as:

$$VSSA = a \cdot f(D) = a/D$$

D is the characteristic size of the particles and “a” is a positive numerical constant *depending on the shape and the density of the particles*.

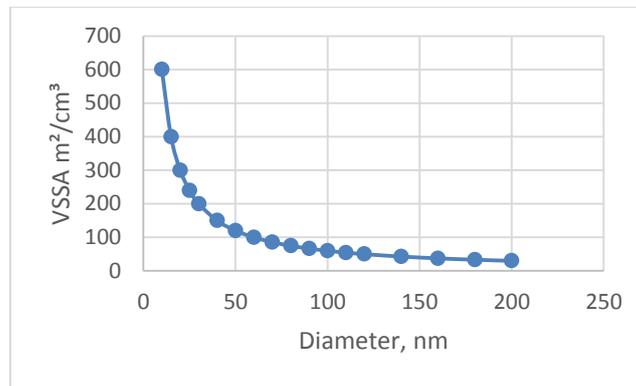


Figure 1 VSSA as a function of D for monodispersed distributions.

The particle size distribution can be transformed into a VSSA distribution by considering the particle size-distribution as **a sum of a series of mono-dispersed distributions of size D, each of them being characterised by a VSSA value a/D and appearing at a frequency representative of the number distribution** (Figure 1), which will then be integrated to calculate the VSSA corresponding to the global sample.

In the case of a normal distribution $D \sim N(\mu, \sigma^2)$, the VSSA can be expressed by:

$$VSSA = \int a \cdot f(D) \cdot N(\mu, \sigma^2) \cdot dD$$

In the case of a lognormal distribution $D \sim \ln N(\mu, \sigma^2)$, the VSSA can be expressed by:

$$VSSA = \int a \cdot f(D) \cdot \ln N(\mu, \sigma^2) \cdot dD$$

In the more general case where the distribution of D is given by F (D), the VSSA is given by:

$$VSSA = \int a \cdot f(D) \cdot F(D) \cdot dD$$

On these bases, VSSA values were calculated for a series of normal and lognormal distributions of particle size, characterized by several μ and σ values. The results are shown in Table 1 and Table 2, and the integration covers the diameter range between 1 and 500 nm considering the spherical particles.

The normal distribution centered on μ theoretically varies from $-\infty$ to $+\infty$, but when applied to particle size distributions, it should be limited to zero, the size being always positive. Taking into account the fact that 99.7% of the distribution is included in the interval $\mu \pm 3\sigma$, the so-called 3 σ - rule can be applied here to consider that this approach is acceptable. However, μ value is much lower than 3σ , (in Table 1), implies a significant fraction of particles with a size of 1 nm. In such a case, the use of a normal distribution is not appropriate.

A log-normal distribution is a distribution of a random variable whose logarithm is normally distributed. Thus, if the random variable D is log-normally distributed, then $Y = \ln(D)$ has a normal distribution. A random variable which is log-normally distributed takes only positive real values. The logarithm can be natural (Napierian) or decimal, but the natural is preferred.

The normal distribution $Y = \ln(D)$ is characterized by its parameters the median μ_y and the standard deviation σ_y . These parameters are of course linked to the characteristics of the distribution of D in the following way:

The median of D = $\mu_D = \exp(\mu_y)$ or $\mu_y = \ln(\mu_D)$

The variance of D = $\sigma_D = [\exp(\sigma_y^2) - 1].\exp(2\mu_y + \sigma_y^2)$

Table 1 VSSA values calculated for normal distributions $N(\mu, \sigma^2)$ of spherical particles; the values higher than the threshold are highlighted in red bold. The grey zone indicates nanomaterials with 50% of their particles below 100 nm. The white zone corresponds to non-nanomaterials according to the particle size distribution criterion but some of them (in red) having a VSSA higher than the threshold.

$\mu \backslash \sigma$	20	30	40	50	60	80	100	120	150
60	119.6	152.2	167.2	166.0	157.6				
70	96.1	120.2	140.3	146.9	144.6				
80	81.1	96.7	116.6	128.1	130.8	123.5			
90	70.6	80.2	97.0	110.5	116.9	115.7			
100	62.8	68.7	81.4	94.9	103.6	107.4			
110	56.6	60.4	69.5	81.5	91.2	98.9			
120		54.1	60.4	70.4	80.7	90.6	91.2		
130		49.2	53.5	61.4	70.4	82.5	85.5		
140		45.2	48.2	54.2	62.0	74.8	79.8	79.4	
150		41.8	44.0	48.5	55.1	67.8	74.2	75.3	
180		34.4	35.3	37.2	40.5	50.3	58.6	63.0	
200			31.4	32.5	34.5	41.7	49.7	55.2	58.2
300				20.6	20.9	22.0	24.2	27.6	33.1

The μ_y values are chosen in order to get a series of μ_D values similar to the μ used in the case of the normal distribution. The values of σ_y will vary between 1 and 0.1 to screen a broad spectrum of standard deviations of the distribution of D. The μ_D value corresponds to the median of the size distribution i.e. 50% in number.

As the calculated VSSA values are proportional to the constant “a” the values in Table 1 Table 2 can be adapted to particle shape “x” by multiplying them by the ratio

$$a_{\text{shape}} \times a_{\text{spherical}}$$

Similarly, the calculations were done assuming a density of 1 g/cm³, the constant “a” could be adapted to any other density value.

By dividing the VSSA values in Table 1 and Table 2 with 60 m²/cm³, it is possible to define an area in the plane (μ, σ) where the VSSA value is higher than the threshold, even if less than 50% of the particles have a size equal to or lower than 100 nm. This is represented in Figure 2 and Figure 3 for normal and lognormal distributions respectively. The 50% threshold of the distribution is used as a criterion to decide if it is a nanomaterial or not.

Table 2 VSSA values calculated for lognormal distributions LN (μ_y, σ_y^2) of spherical particles, with $\mu_y = \ln(\mu_D)$; the values higher than the threshold are highlighted in red. The grey zone indicates nanomaterials with 50% of their particles below 100 nm. The white zone corresponds to non-nanomaterials according to the particle size distribution criterion but some of them (in red) having a VSSA higher than the threshold.

σ_y \ μ_D	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
70	86.0	87.4	89.6	92.8	97.0	102.0	108.3	116.7	127.5	140.7
80	75.4	76.5	78.5	81.2	84.9	89.5	95.0	102.2	111.4	122.9
90	67.0	68.0	69.7	72.2	75.5	79.6	84.6	90.9	98.9	109.0
100	60.3	61.2	62.8	65.0	68.0	71.7	76.2	81.8	89.0	97.9
110	54.8	55.6	57.1	59.0	61.8	65.2	69.3	74.4	80.8	88.9
120	50.3	51.0	52.3	54.2	56.6	59.8	63.5	68.2	74.0	81.3
130	46.4	47.1	48.3	50.0	52.3	55.1	58.6	62.9	68.2	74.9
140	43.1	43.7	44.8	46.4	48.5	51.1	54.4	58.3	63.2	69.4
150	40.2	40.8	41.8	43.3	45.3	47.7	50.7	54.3	58.9	64.7
180	33.5	34.0	34.9	36.0	37.6	39.5	41.9	45.0	48.7	53.5
200	30.2	30.6	31.4	32.4	33.7	35.3	37.5	40.2	43.6	47.9

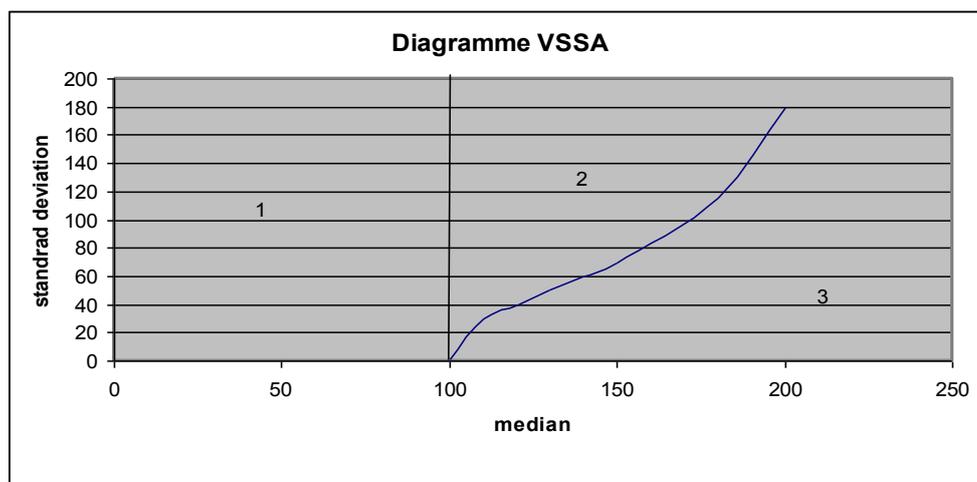


Figure 2 Plane (μ, σ) for normal distributions, separated in three zones. Zone 1: VSSA higher than threshold corresponding to nanomaterials; zone 2: VSSA higher than threshold corresponding to non-nanomaterials; zone 3: VSSA lower than threshold corresponding to non-nanomaterials.

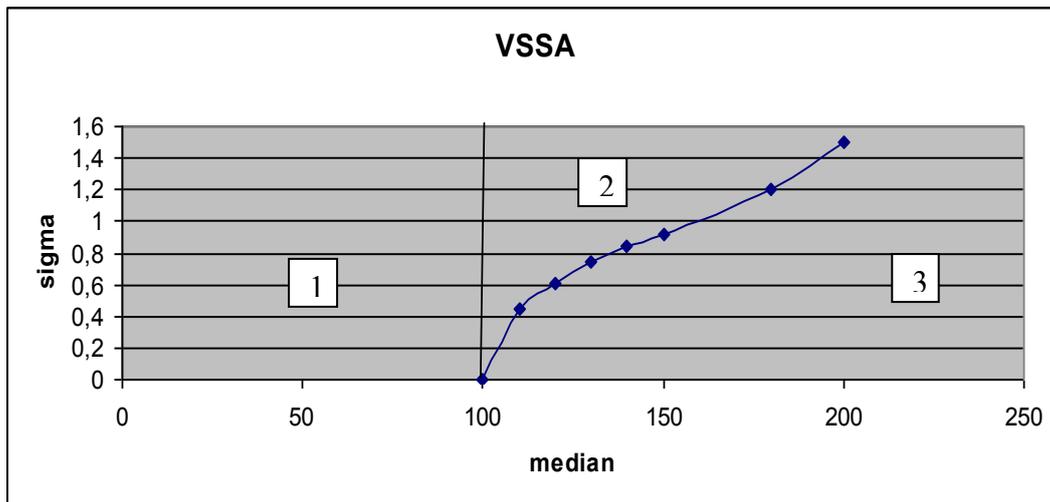


Figure 3 Plane (μ_D , σ_y) for lognormal distributions, separated in three zones. Zone 1: VSSA higher than threshold corresponding to nanomaterials; Zone 2: VSSA higher than threshold corresponding to non-nanomaterials; Zone 3: VSSA lower than threshold corresponding to non-nanomaterials

The model also allows to calculate the part of VSSA generated by the particles with a characteristic size lower than or equal to a given value “d” of the size. The fractions are obtained by limiting the integration of the distribution between 1 nm and 100 nm and by comparing the results to the full integral.

The results are illustrated on Figure 4 for a series of lognormal distributions characterised by various μ_D and σ_y values.

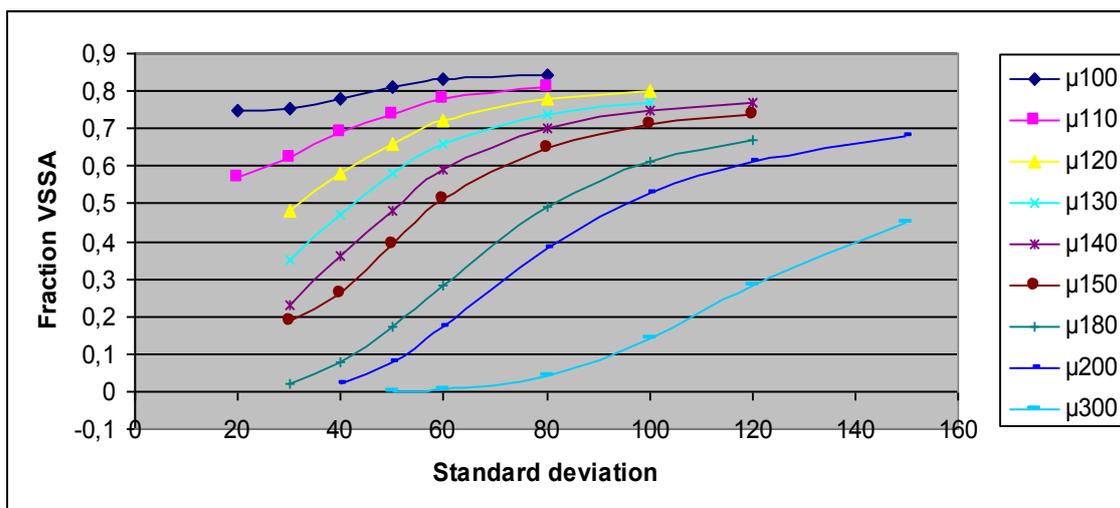


Figure 4 Variations of VSSA fractions generated by nanoparticles (with a size lower than 100nm) as a function of the standard deviation σ_y of the lognormal distribution (μ in nm).

It is interesting to use the formula to calculate the percentage or fraction of nanoparticles (below 100 nm) present in a series of lognormal distributions characterized by various μ_D and σ_y values. The corresponding results are illustrated in Figure 5. By definition, 50% of the particles are nanoparticles when the normal distribution is centred at $\mu_D = 100$.

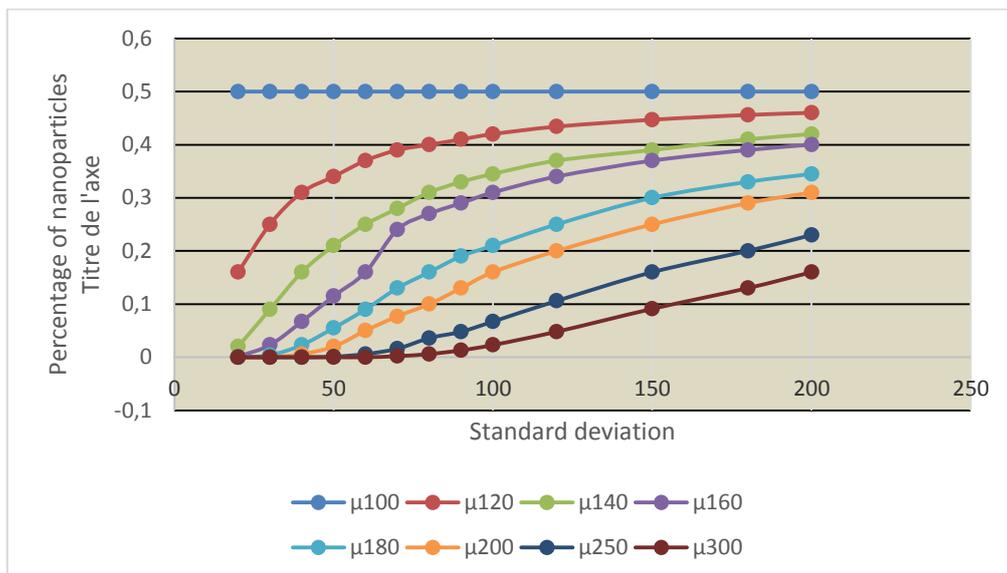


Figure 5 Fraction of nanoparticles (with a size lower than 100 nm) as a function the lognormal distribution parameters: the median μ_D (expressed in nm) and the standard deviation σ_y .

As the results show, the VSSA fractions generated by the nanoparticles with a size lower than 100 nm is always higher than the fractions of the particle number in the nano-range. This is due to the fact that the surface area of the particles increases when the particle size decreases.

- **Bimodal particle size distributions**

There are some concerns about the application of VSSA approach to the bimodal distribution of particles. It appears that any combination of at least 50% in number of a lognormal distribution characterised by a μ value less than 50 nm and any other lognormal distribution characterised by a μ value higher than 100 nm, will lead to a VSSA value greater than the threshold, even if there is less than 50% number of nanoparticle in the total sample.

However, when the size of the nanoparticles is larger than 50 nm, a 1:1 mixture of monodispersed nanomaterial and monodispersed non-nanomaterial gives a VSSA value under the threshold, as illustrated in Table 3. This indicates some limitation in the use of the VSSA for bimodal distributions.

- **Agglomerates and aggregates**

The terms agglomerates and aggregates are defined as follows (the EU definition and the ISO Technical Specification (TS 27687))

Agglomerate means a collection of weakly bound particles or aggregates where the resulting external surface area is similar to the sum of the surface areas of the individual components.

Aggregate: means a particle comprising strongly bound or fused particles where the resulting external surface area may be significantly smaller than the sum of the calculated surface areas of the individual components

Table 3 VSSA values for mixtures of two monodispersed distributions of spherical particles, one with a size in the nano-range and the other with a size outside the nano-range.

Sizes	200 nm	400 nm	800 nm	1000 nm	1200 nm
25nm	135	127,5	123,8	123,2	122,5
50nm	75,1	67,5	63,8	63,2	62,5
75nm	55	47,3	43,8	43,2	42,5
99nm	45,5	37,8	34	33,3	32,8

For the definitions, it is clear that the thresholds of VSSA can theoretically be applied to agglomerates but not to aggregates. Even if free nano-particles have a tendency to form agglomerates via weak forces, they can be easily separated and their surface remains accessible to adsorbates. Consequently the VSSA approach is easily applicable, and the accessible surface of the particles in agglomerates being the same as in a set of free particles surface.

Free nanoparticles can also form aggregates either in suspension or during drying and/or thermal treatment and may form irregular clusters, flocks, or aggregates of various shapes as illustrated on Figure 6 hereafter.

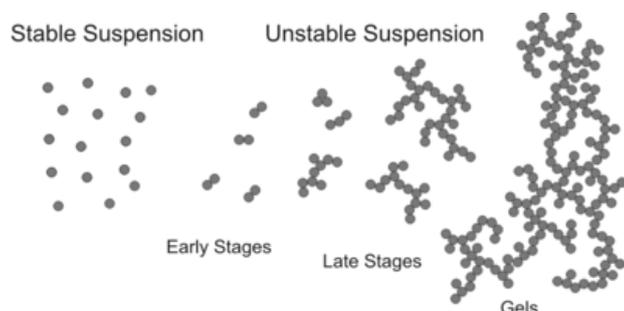


Figure 6 Illustration of the first stage of particles aggregation in a suspension

To assess the available surface during the aggregation process, we consider the partial coalescence of two identical spherical particles forming a grain boundary. When there is no coarsening of the particles during the aggregation stage, there is almost no variation of the specific surface area. This change remains within the precision limits of surface area measurements.

When the sintering process continues and the particles fuse, the resulting external surface area may be significantly lower than the sum of the calculated surface areas of the individual surfaces and cannot be used to assess the particle size. Hence, the material may be considered as nanostructured with “internal porosity” and the material may also be classified as nano according to the EC definition. Even if the surface area after sintering is decreasing, the in-depth analysis of the adsorption isotherms obtained at different aggregation stages can provide interesting information on the internal porosity and the external surface of the particles or aggregates. It gives the possibility to assess the texture from free nanoparticles and nanoporous materials like zeolites.

2.3.1.4 Discussion

- **Effect of particle shape**

The nitrogen adsorption isotherms are used to determine the VSSA, by measuring the total accessible surface area of the various particles. If the VSSA is estimated from the particle size distributions (obtained by electron microscopy) of non-spherical particles, Feret diameter is recommended to access the correct particle size. The particle size distribution was measured by centrifugation or light scattering; the particles behave as spheres corresponding to their smallest size, the threshold from the similar shape should be considered. It implies that the shape of particles, which may vary as a function of the synthesis method, is known. Even if the crystallographic data can provide a first idea of the possible shape, the key method to determine the appropriate shape is by electron microscopy images. These qualitative pictures are common information available for this range of particle sizes.

- **Effect of polydispersity**

As shown in this study, the VSSA value also depends on the particle size distribution. Calculations were made for normal and lognormal distributions, characterized by various median and standard deviation values.

The resulting VSSA, called total VSSA, appears to be overprotective because it identifies non-nanomaterials as nano- (see zone 2 in Figure 2 and Figure 3) in particular for particles of broad particle size (i.e. high standard deviation). It may lead to misinterpreting powders of non-nanomaterials contain nano characteristics.

In this study, an analytical approach is used, expressing VSSA as the sum of individual VSSA corresponding to each particle size of the number distribution. This leads to the following formula as explained above:

$$\text{VSSA} = \int a \cdot f(D) \cdot N(\mu, \sigma^2) \cdot dD$$

$$\text{VSSA} = \int a \cdot f(D) \cdot \ln N(\mu, \sigma^2) \cdot dD$$

For normal and lognormal distribution respectively.

In other words, the model presented in this report considers that each mono-dispersed particle is characterized by its surface/volume ratio $S_i/V_i = \text{VSSA}_i$ which is expressed as $f(D) = 1/D$.

The sum of individual VSSA_i with their relative frequencies F_i will give the total VSSA of the monodispersed particle size distributions. The frequencies reflect the normal or lognormal character of the distribution:

$$(\text{VSSA})_{\text{total}} = F_1 \times S_1/V_1 + F_2 \times S_2/V_2 + \dots + F_n \times S_n/V_n = \text{Sum on } i (F_i \times S_i/V_i)$$

$$(\text{VSSA})_{\text{total}} = F_1 \times \text{VSSA}_1 + F_2 \times \text{VSSA}_2 + \dots + F_n \times \text{VSSA}_n = \text{Sum on } i (F_i \times \text{VSSA}_i)$$

Unfortunately, the conclusions made in this study are not in-line with the findings of the second JRC report (Roebben et al. 2014). The model considers experimental BET as the (accessible-) surface area of all the particles, divided by the volume of all the particles (included in the measured density). Therefore, the resulting VSSA is the ratio of the surface area of all particles divided by the volume of all particles. As a consequence of their modeling approach, they express VSSA in the following way

In the case of a normal distribution $D \sim N(\mu, \sigma^2)$, the VSSA can be expressed by:

$$VSSA = \int s \cdot S(D) \cdot N(\mu, \sigma^2) \cdot dD / \int v \cdot V(D) \cdot N(\mu, \sigma^2) \cdot dD$$

In the case of a lognormal distribution $D \sim \text{Ln } N(\mu, \sigma^2)$, the VSSA can be expressed by:

$$VSSA = \int s \cdot S(D) \cdot \text{Ln } N(\mu, \sigma^2) \cdot dD / \int v \cdot V(D) \cdot N(\mu, \sigma^2) \cdot dD$$

where $S(D) = D^2$, $V(D) = D^3$, s and v being constant depending on the shape of the particle.

In practice the VSSA will be calculated by

$$(VSSA) = s (F1 \times S1 + F2 \times S2 + \dots + Fn \times Sn) / v (F1 \times V1 + F2 \times V2 + \dots + Fn \times Vn)$$

The shape constants are the following:

Spherical-like particle: $s = \pi$ and $v = \pi/6$.

Fibre like particle: $s = \pi$ and $v = \pi/4$

Sheet like particles: $s = \pi$ and $v = \pi/2$

In the Roebben et al. (2014) approach, the calculated VSSA corresponds to the inverse of the Sauter means diameter, i.e., the VSSA is the weight averaged value of the surface area distribution. The model provides a weight averaged VSSA in which the weight of large particles is critical, leading to a lowering of the VSSA values at the broad particle size distribution. However, the model developed in this Deliverable D2.11, we consider particle size contributes to its individual weight.

Obviously, the two models will give different VSSA values in particular for broad particle size distributions. The total VSSA based on the VSSA concept being always higher than the weight averaged VSSA.

In the JRC report (Roebben 2014), it is written:

Despite the fact that VSSA of a single particle increases more rapidly to the low side of 100 nm than it decreases to the high side of this threshold symmetric broadening of the number-based particle size distribution (PSD), while maintaining a median size of 100 nm, will reduce the measured VSSA.... Most asymmetric broadening functions (e.g. lognormal) would also lead to reduced overall VSSA values for a median size of 100 nm. This is because the contribution of the smaller particles to the overall surface area and to the overall volume diminishes very rapidly with decreasing particle size.

There is a clear contradiction between the starting sentence and the last justification of the decrease of VSSA with a broadening of the distribution. Recognizing the contribution of small particles is higher than the larger, their influence on the calculated VSSA is lower than the larger ones.

The model developed in this study confirms the higher contribution of small particles to the VSSA as foreseen by the $1/D$ dependence of VSSA, with D being the size characteristic of the particles.

Figure 7 shows the variation of the VSSA with the standard deviation of a normal and a lognormal distribution characterized by a median of 100 nm. Series 1 in blue corresponds to this study's model (total VSSA) and the series 2 in orange to the JRC model (weight averaged VSSA). The decrease in the VSSA for the log-normal distribution (compared to the normal distribution), is an excellent illustration of the over-importance of the large particles in the JRC model.

- **Bimodal distributions**

The use of total VSSA for bimodal distribution particles may have difficulties in identifying nanomaterials. For example, by combining two populations, one with a median value between 100 and 200 nm and the other with a median value lower than 100 nm, it is not possible to identify the nanomaterial as a mixture in equal number proportion of mono-dispersed nanoparticles. This is even worse if the size of the particles increases.

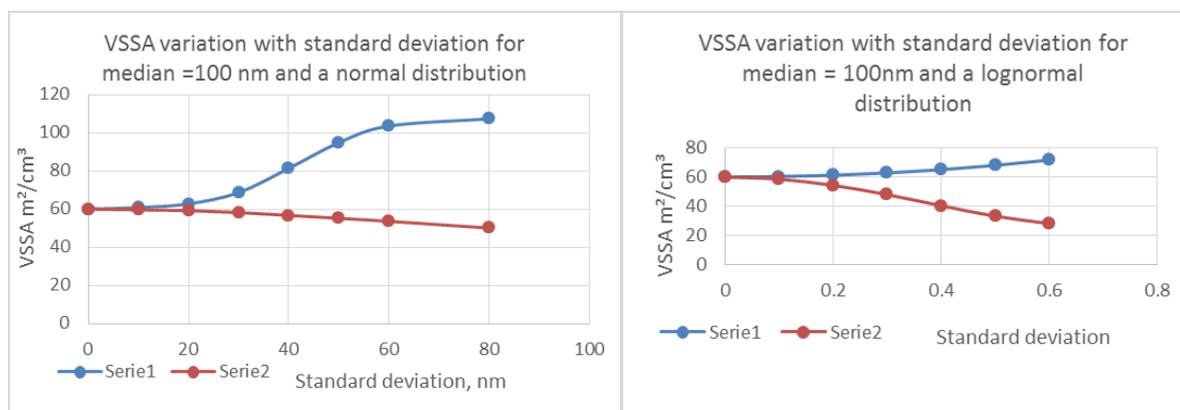


Figure 7 Normal distribution and log normal distribution. Variations of the VSSA with standard deviation for distribution characterised by a median value of 100 nm; in blue total VSSA, in orange: weight averaged VSSA.

However, the limitations are even worse if weight averaged VSSA model applied to bimodal distributions. For an example, both VSSA models used for a series of theoretical 50/50 % number mixtures of particles with a size below 100 nm and particles with a size higher than 100 nm. The results are shown in Figure 8.

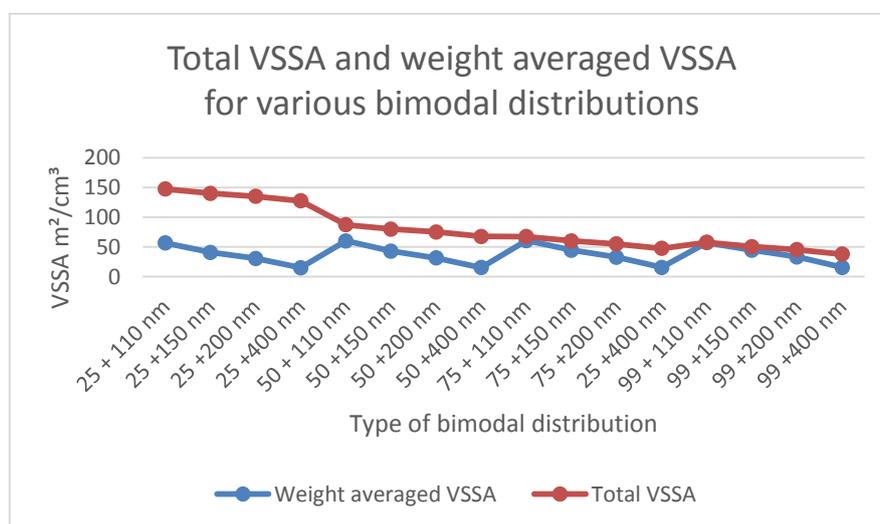


Figure 8 Comparison between the total VSSA and the Weight averaged VSSA for various 50N50 bimodal particle size distributions indicated on the x axis. Red line: total VSSA values, Blue line: weight averaged VSSA values.

As shown in Figure 8, all weight averaged VSSA values are much lower than the total VSSA values for the mixtures, and are below the threshold, indicating that the model is not able to identify nanomaterial of interest.

- **Agglomerates**

The VSSA approach may be applied to agglomerates due to the accessibility of the surface of individual particles. One can assume that there is almost no variation of the surface area of agglomerates compared to the free particles, and consequently, the VSSA can be applicable in a reliable way.

It is interesting to point out that, due to the overprotective character of the total VSSA it can be a useful tool to identify “non-nano” materials. If the total VSSA value is below the threshold, it is a clear indication that the powder is not a nanomaterial. Hence it can be used as a screening tool to eliminate particles of non-nanomaterials. If the VSSA value lower than the threshold, it can indeed be considered as reliable non-nano criteria; the effect of the polydispersity of a particle size increases the VSSA value much more than the aggregation of the particles reduces it. This conclusion is not valid for the weight averaged VSSA value.

2.3.1.5 Conclusion of the theoretical study

A criterion based on the total VSSA to identify nanomaterials has been developed in as an outcome of the NanoReg, Deliverable D2.11 and it can be applied to several nanomaterials with the following several conditions:

- The threshold should be adapted to particle geometry; this implies to have a qualitative electron microscopy picture to choose the appropriate shape factor.
- The particle size distribution should be mono-modal. Limitations occur in the case of bimodal distributions.
- Only the external surface of the particles is linked to their size and hence the surface area.

In most cases, the total VSSA criterion is overprotective for the 50% threshold applied to the number distribution of particle sizes. It means that having less than 50% of the particles below 100 nm but characterized by a VSSA higher than the threshold, are wrongly considered as nanomaterials. The total VSSA approach will lead to many false positive nanomaterials.

On the other hand, if VSSA is below the threshold, the sample can be considered as a non-nanomaterial. If the distribution of the primary particles is mono-modal, there is no false negative identification for free, agglomerated or softly aggregated samples (Figure 6). This may be a useful and easy tool to identify non-nanomaterials.

When the aggregation is much higher by their broad particle size distributions, the sample can be considered as nanostructured or nano-porous. In that case, the pores size and volume could be interesting parameters to identify nanomaterials together with VSSA.

2.3.2 Experimental Approach

The VSSA concept assumes that the particles are spherical, non-porous and monodispersed. The above theoretical study shows that the VSSA concept may be applied to non-spherical, polydisperse non-porous particles by considering normal or lognormal particle size distributions.

In practice, the question is: “how to measure the VSSA?” It was suggested to use the BET method to measure the total surface area and to divide it by the particle density. However, the BET specific surface area takes into account the internal porosity of the particles and consequently, is not linked to the particle size. Only the external surface of the particles is linked to their size and should replace the BET value.

2.3.2.1 Measurement of internal and external surface areas of the particles

Measurement of the internal and external surface of the particles is by an in-depth analysis of the nitrogen adsorption isotherms. Such a methodology was previously developed and can be applied even to particles in the nano-range. A brief explanation of the method is included details in the D2.11. Protocol (see Annex 1).

This method is easily applicable to the dry powders without any modification. For the solid suspended in liquid like colloids, the N₂ adsorption isotherm cannot be directly used. The suspension should be dried to collect the solid part. The drying may modify the degree of agglomeration of the particles but, in general, the size of the primary particles will not be affected if the drying conditions are smooth.

2.3.2.2 Sample preparation and measurement conditions

The procedure for measuring the surface area by nitrogen adsorption isotherms is according to ISO (2006, 2007 and 2010) and IUPAC (1985). The most critical step in the measurement is the outgassing stage, i.e. to clear the adsorbent surface to any adsorbed molecules before the measurements.

The outgassing process of the solid sample can be performed at room temperature, or at a higher temperature to promote desorption of strongly adsorbed species. The pre-treatment conditions must remain sufficiently mild to avoid any modification of the textural characteristics of the sample but severe enough to obtain a good surface clean-up. It is recommended to perform the pre-treatment in the cell used to carry out the adsorption. Whatever the temperature, the solid must be submitted to a minimum vacuum of 10^{-2} Nm⁻² i.e. 10 mPa during at least one hour. Such conditions are readily achieved with the aid of conventional vacuum equipment, usually a combination of a rotary and diffusion pump. In general, the lower the temperature, the longer the outgassing process should be.

For more detailed description of the isotherms, its always recommend using as many experimental points as possible.

Experimental conditions may vary depending on the instrument type and laboratory conditions. It has also been shown that the importance of the outgassing conditions is indeed essential for measuring the density of samples by helium pycnometer (D2.9).

Herein, we used three laboratories for reproducibility of the results and to identify the effect the measurement conditions, summarized below in Table 4.

Table 4 Experimental conditions used in the three laboratories

	Lab 1	Lab 2	Lab 3
Apparatus	Micromeritics ASAP2420	Autosorb IQ2 analyzer (Quanta chrome)	Micromeritics TriStar II 3020 V1.04
Degassing temperature	30°C	Room temperature	Room temperature 20-22 °C
Degassing vacuum	2.6 μbar	2.6 mbar	30 – 50 mbar
Degassing time	15 h or 24 h	1 hour	4-5 hours

a) The BET method

Surface areas are measured by the (BET) method at a relative pressure $p/p_0=0.05-0.3$, assuming a cross-sectional area of 16.2 \AA^2 for adsorbed nitrogen.

The BET equation contains two key parameters, the first one being the volume V_m of the monomolecular layer covering the surface of the particles and the second one the C_{BET} value characteristic of the intensity of the adsorbate- adsorbent interactions. As the C_{BET} parameter is related to the differential heat of adsorption, the stronger the adsorbate-adsorbent interactions, the higher the C_{BET} -value, whatever the type of porosity present in the solid.

b) The t-plot approach

The basic principle of the t-method is to compare the nitrogen adsorption isotherm obtained for a given porous solid with a particular reduced form of a standard isotherm (the so-called universal t-curve) corresponding to a non-porous solid of the same. The nitrogen volume, v_a adsorbed at a relative pressure p/p_0 on a given sample is plotted as a function of the thickness, t , of the adsorbed layer, as given by the "universal t-curve" for the same relative pressure.

But the reference t-curve depends on the intensity of adsorbent-adsorbate interactions as illustrated by the C_{BET} constant value. The t-plot approach should then be amended to take into account the adsorbent-adsorbate interaction. Various reference t-curves should be used depending on the C_{BET} value.

Through the so amended v_a -t-plot, valuable information can be obtained about the porous structure of the adsorbent. Several interesting pieces of information can be derived from the so amended t-plot, in particular, the total surface area S_t which is comparable to BET surface area S_{BET} as well as the external and internal surface areas of the particle S_w and S_μ . Moreover, the shape of these plots combined with the shapes of the nitrogen adsorption isotherms is also very informative. Several examples are given in section 6.3.4.6.

Overall, an in-depth analysis of the isotherms and the corresponding t-plots may provide an interesting insight into the texture and the nano character (if any) of the sample. Of course, in a few cases, some ambiguities could remain that can be solved by a qualitative electron microscopy picture.

2.4. Results

a. Nature of the samples

Different types of samples are tested in this study such as TiO₂ nanomaterials (NM-100 and NM-103), ZnO nanomaterial (NM 110), synthetic amorphous silica nanomaterials (NM-200 and NM-203) and single wall carbon nanotubes (NM 411) obtained from the nanomaterials repository of the EC Joint Research Centre (European Commission 2014). Two ZnO grades (Pharma and Nano) kindly provided by Umicore, two industrial coated rutile TiO₂ grades H1 and H2 kindly provided by Huntsman and porous silica (MCM 41) synthesized and provided by one of the authors (RA) are also included in this study.

b. Repeatability and reproducibility of BET and total surface areas

It is important to check the reliability of the surface area measurements by considering the repeatability and the reproducibility of the results. The repeatability of the BET surface area was first checked in Lab1 by looking at the possible effect of the sample mass on the measured value. The results presented in Table 5 indicate an excellent repeatability of the method in this laboratory.

Table 5 BET surface area obtained on various sample weights of two ZnO powders.

Sample mass, mg	200	200	400	400	725	725	1000	1000	2000	2000
ZnO Pharma	5.4	5.2	5.4	5.2					5.2	5.2
ZnO Nano	22.3	23.0	22.4	22.6	22.7	22.3	22.6	22.7		

Table 6 confirms that the repeatability of the surface areas (BET and St) is quite satisfactory within each laboratory, except for the sample NM 200 in Lab 3 for which the variations are more significant.

Looking at the reproducibility of the results, we consider the replicate measurements made by different analysts, working in different laboratories, using different equipment. The results presented in Table 6 are showing a reproducibility of about 7% between Lab 1 and Lab 2 values for S_{BET} and S_t . The Lab 3 results differ of about 15% significantly from the two others especially for NM100 and both ZnO samples. These higher variations in repeatability and reproducibility could come from the degassing conditions, which are less severe in Lab 3 compared to Lab 1 and 2 as shown in Table 6.

2.4.1 Internal and external surface of the particles

For non-porous nanoparticles, the total surface area of the particles (S_{BET} or S_t) can be used to calculate the corresponding VSSA values. For porous, nanostructured or coated nanoparticles, only the external surface of the particles should be considered to calculate the VSSA. The internal porosity or the porosity created by the coating can be determined by analyzing the low-pressure area of the t-plot (low value of t).

It implies to have a sufficient number of experimental points in this low-pressure region and to use the appropriate standard isotherm as described before. Moreover, small pores characterize the internal porosity; it is essential to degas under vacuum conditions before the measurements. If the degassing conditions are not sufficient and/or if the number of experimental points in the low-pressure region is not enough, this internal porosity will not appear on the t-plot. This is exemplified in the Figure 9 and Figure 10 hereafter for the TiO₂ H1 sample.

Table 6 Summary of the SBET and St surface areas obtained in the three laboratories on all the samples.

Samples	Laboratory 1		Laboratory 2		Laboratory 3	
	S _{BET} m ² /g	S _t m ² /g	S _{BET} m ² /g	S _t m ² /g	S _{BET} m ² /g	S _t m ² /g
NM 100	9.8	10.0	10.3	10.5	7.5	7.4
	9.8	10.1	10.3	10.7	7.9	7.9
			10.2	10.7	7.4	7.8
NM 103	52.0	53.4	50.7	52.5		
	52.0	53.4				
NM 110	11.7	11.9				
	11.0	11.2				
NM 200	171.4	172.2	160.9	164.5	158.7	150.8
	171.9	173.4	162.5	165.8	172.0	177.9
			163.9	165.7	156.8	164.4
			161.7	165.7	143.2	164.4
NM 203	194.4	197.2	186.4	208.8	195.9	194.0
	197.8	200.7	199.2	193.4	190.4	205.0
					193.8	193.4
					189.2	203.0
TiO2 H1	34.5	35.6	34.8	36	32.1	33
TiO2 H2	14.5	14.9	14.4	15.5	11.2	11.4
NM 411	816.7	825	766.4	812	822	814
MCM41	835.6	836	850.3	859	602.7	608
ZnO pharma	5.3	5.3	5.4	5.6	4.3	4.5
	5.2	5.3				
ZnO nano	22.5	22.7	21.4	22.2	19.1	19.9
	22.8	23.0				

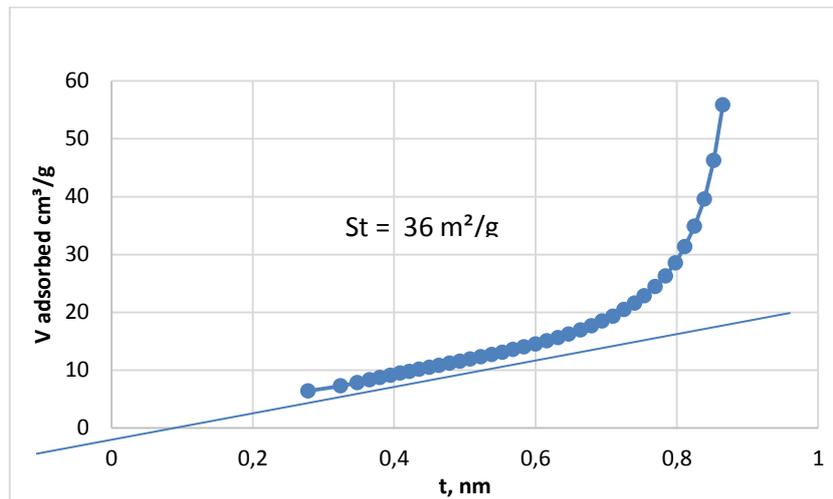


Figure 9 t-plots with insufficient number of experimental points in the low pressure (or t) region to show internal surface area (S_{μ}) of the sample, in this case due to coating. The external surface area of the particle (S_w) is obtained by subtracting the internal (S_{μ}) from the total (S_t) surface area.

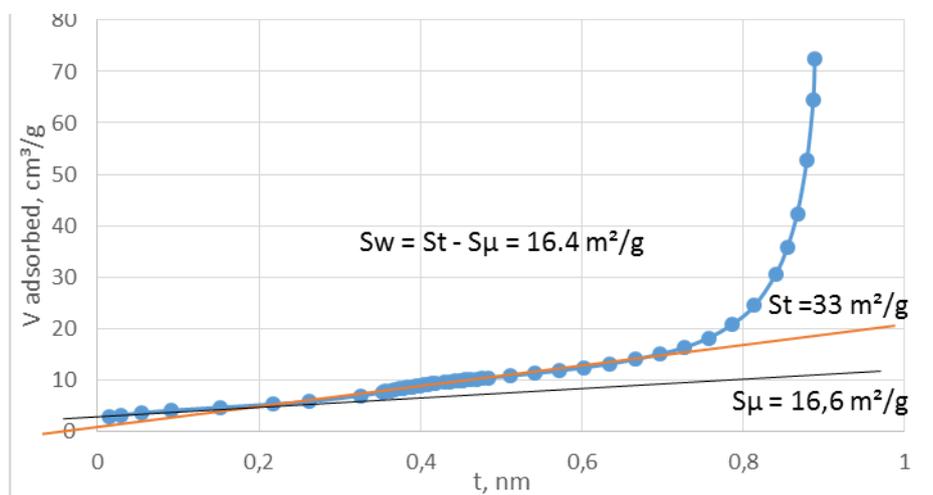


Figure 10 t-plots with sufficient number of experimental points in the low pressure (or t) region to show internal surface area (S_{μ}) of the sample, in this case due to coating. The external surface area of the particle (S_w) is obtained by subtracting the internal (S_{μ}) from the total (S_t) surface area.

Similarly, the precision in determining the internal surface area depends on the number of experimental points in the low pressure region as illustrated on Figure 11 and Figure 12 hereafter for the carbon nanotube sample NM-411.

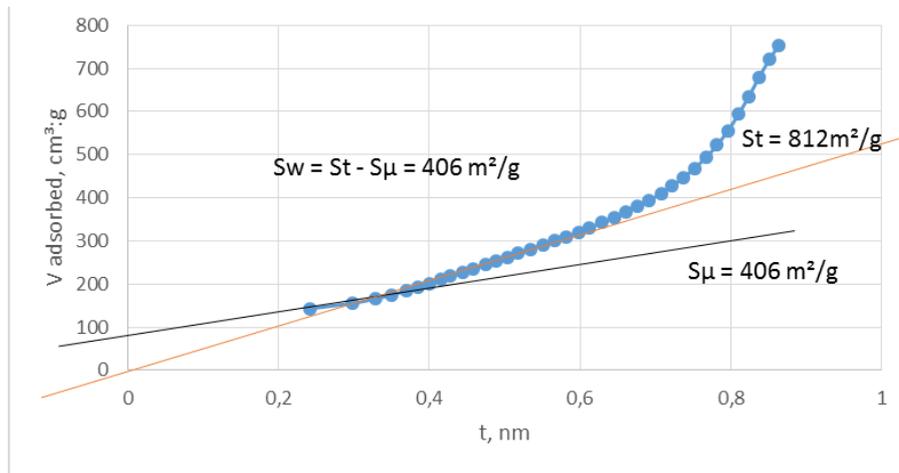


Figure 11 t-plot with insufficient number of experimental points in the low pressure (or t) region to measure the internal surface area (S_{μ}) of the sample with enough precision; in this case internal surface comes from hollow nanotubes. The external surface area of the particle (S_w) is obtained by subtracting the internal (S_{μ}) from the total (S_t) surface area.

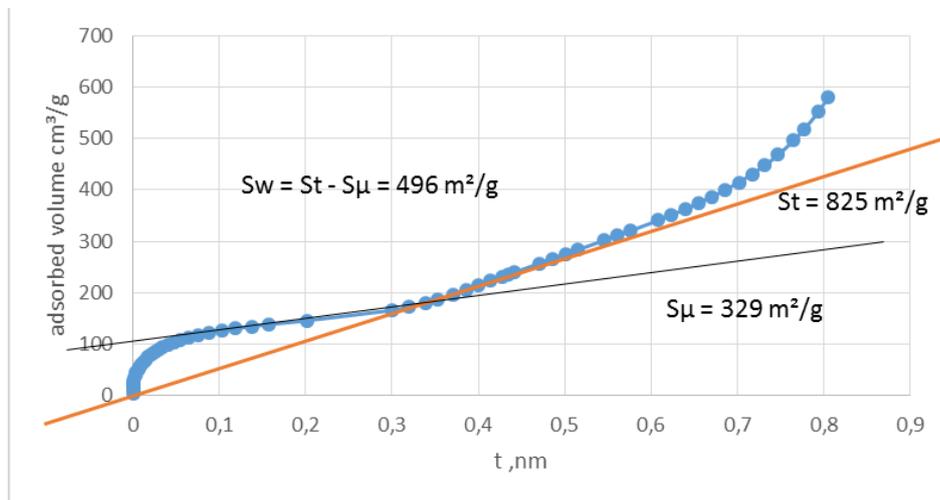


Figure 12 t-plots with sufficient number of experimental points in the low pressure (or t) region to measure the internal surface area (S_{μ}) of the sample with enough precision; in this case internal surface comes from hollow nanotubes. The external surface area of the particle (S_w) is obtained by subtracting the internal (S_{μ}) from the total (S_t) surface area.

The t-plot can also give information on the size of the aggregates of nanoparticles. In the case of the porous silica sample, the t-plot shows that the nanoparticles have an internal porosity developing a surface S_{μ} and an external surface S_w , the total surface S_t being the sum of S_w and S_{μ} . They also form aggregates with an external surface S_{aggr} , as illustrated in Figure 13. If the particles are assumed to be spherical with a density of 2.1 g/cm^3 , the size of the elementary particles estimated to be about 7 nm forming aggregates of about 33 nm which are not accessible by the t-plot.

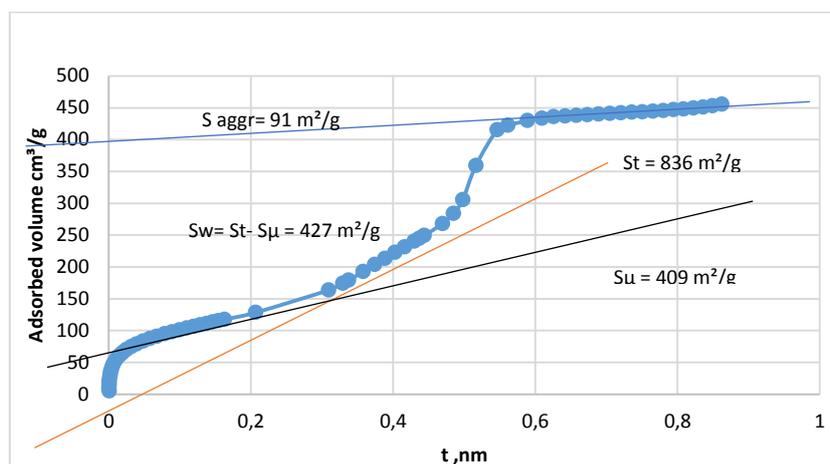


Figure 13 t-plot obtained on the porous silica sample MCM 41, showing the internal surface of the particle, S_{μ} , the total surface of the particles S_t and the external surface of the aggregates, S_{aggr} .

These examples illustrate how the t-plot approach can provide interesting information on the texture of solids and the sizes of the particles and aggregates.

2.4.2 Identification of nanomaterials based on experimental VSSA

To estimate the VSSA values corresponding to the samples, the total (S_{BET}) and external (S_w) surface areas were calculated by averaging the values obtained in the three laboratories. These values are reported in Table 7 hereafter together with the density values.

The samples identified as non-nanomaterials are highlighted in grey in Table 7. It is interesting to note that the VSSA approach can distinguish nano and non-nano characteristics of zinc oxides and titanium dioxides. Also, there is a consistency between the three laboratories in the identification of nano and non-nano materials if nearly spherical particles are assumed (i.e. according to the EU definition: $VSSA < 60 \text{ m}^2/\text{cm}^3$).

2.4.3 Comparison with electron microscopy data

2.4.3.1 Conceptual approach

According to the European Commission recommendation, the key criteria to identify a nanomaterial is based on the number particle size distribution: a nanomaterial has 50% or more particles with a size between 1 nm and 100 nm. Transmission electron microscopy (TEM) coupled with image analysis is considered as the best viable technique to assess the number particle size distribution and has the advantage to visualize and measure primary particles (PPs) in complex aggregated and agglomerated powdered nanomaterials. As the VSSA approach is considered as a possible surrogate of the approach to the number particle size distribution, it is essential to link the VSSA threshold and the 50% criterion to the particle size distribution.

In the theoretical approach of this study, the potential influence of the morphology/shape of the particle as well as the effect of the particle size distributions on the threshold value and the VSSA measurement was discussed. A model to calculate the VSSA value from a given particle size distribution was developed, making a possible link between the two types of criteria proposed to identify nanomaterials, i.e. VSSA versus 50% of particles with a size lower than 100 nm.

To validate the model and to check the compatibility of the two criteria, (VSSA and particle size distribution), to identify nanomaterials, both types of measurements were carried out on a series of samples. This experimental approach is presented in the next sections.

Table 7 VSSA values by using the total (SBET) or the external (Sw) surface area

Sample	S _{BET} m ² /g	S _w m ² /g	Density g/cm ^{3*}	VSSA m ² /cm ³	
				Ex S _{BET}	Ex S _w
ZnO nano	21.7	12,8	5.6	121.5	72.2
ZnO non nano	5.1	2.7	5.6	28.6	15.2
NM-100 TiO ₂	10.2	5.5	4.23	43.1	23.3
NM-103 TiO ₂	52.2	18.1	4.23	220.8	76.6
NM-200 SiO ₂	170	162	2.2	374	356.4
NM-203 SiO ₂	197	108	2,2	433	237.6
TiO ₂ H1	34.3	18.2	4.23	145	77.00
TiO ₂ H2	13.7	6.5	4.23	57.9	27.5
NM-411 SWCNT	801	483	2.05	1642	990.2
MCM 41 SiO ₂	845	402	2.2	1859	884.4

**Material densities, for TiO₂ rutile (4.23 g/cm³), for ZnO (5.6 g/cm³) and for synthetic amorphous silica (2.2 g/cm³) are taken from OECD Database as reasonable proxies.*

2.4.3.2 Use of TEM average values

To start the comparison, we refer to the recent work of the Task 2.10 in which the number particle size distributions on several of the nanomaterials were determined. There is two titanium dioxide (NM 100 and NM103) and two silica (NM200 and NM203) whose characteristics are available at JRC (EC 2014).

The particle size obtained by TEM are shown in Table 8. The median values are noted D_p if free primary particles (PP) are considered alone and D_{pt} if all the particles are taken into account, including those in small aggregates. The corresponding mode of the distributions, as well as the full width at half maximum (FWHM), are also given in the table. To calculate the VSSA from the TEM data, all the particles are assumed to be spherical (the TEM images showing nearly spherical particles) with a total diameter D_{pt} including small aggregates and multiplied with S_{BET} by the density of the sample. The S_{BET} surface can also be used to evaluate the particle size by assuming spherical particles. This assumption is justified in this case as the TEM images showing nearly spherical particle.

Table 8 Comparison of data obtained by TEM and nitrogen adsorption on four nanomaterials. The sources of the data are indicated in the table. The density used to calculate the VSSA: for TiO₂ anatase (3.9 g/cm³), TiO₂ rutile (4.23g/cm³) and synthetic amorphous silica (2.2 g/cm³). These density values are taken from OECD database as reasonable proxies. FWHM = full width at half maximum.

Method	Sample	NM-100	NM-103	NM-200	NM-203
TEM	D _p = median PP, nm from **	110	25	18	25
	D _p = median PP, nm *	114.6	18	23.3	13.8
	D _{mp} = mode PP, nm *	55	21	15	11
	FWHM _p , nm *	42	7	10	7
	D _{pt} = median total, nm *	126.6	21	22.2	15
	D _{mt} = mode total nm *	63	18	17	12
	FWHM _t , nm *	108	19	24	11
	VSSA total, m ² /cm ³ *	47.6	285.7	270	400
ADS	S _{BET} m ² /g from **	10	51	189	204
	VSSA from S _{BET} from **	39	216	416	449
	D _p nm, from S _{BET} from **	153	28	14	13
	S _{BET} m ² /g this study	10.1	51.6	166.3	193.3
	VSSA from S _{BET} this study	39.4	218	366	425
	D _p nm, from S _{BET} this study	152	27.5	16.4	14.1

** Data from Nanogenotox (2013) * Data from Task 2.10

From Table 8 it can be concluded that:

- There is a quite good agreement between the S_{BET} values and the particle sizes obtained in this study and the values reported by the Nanogenotox project.
- There is a good agreement in the particle sizes obtained by Nanogenotox project and Task 2.10
- The experimental VSSA approach calculated from the measured BET surface areas identifies the same materials as nanomaterials as the TEM approach.

2.4.3.3 Use of particle size distribution

In the earlier section, it is assumed that all the particles have the same diameter as the median of the distribution. However, the particles are not monodisperse and are not spherical. Based on the particle size distribution obtained by electron microscopy with an average particle shape, it is possible to calculate a more realistic VSSA value corresponding to the total sample. The calculated value will be compared to VSSA calculated from the specific surface areas measured via nitrogen adsorption isotherms. The characteristic parameters of the number particle size distribution of the four samples are reported in Table 9.

To calculate the VSSA values corresponding to the distribution parameters, we can assume either normal or lognormal distributions and calculate μ and σ values with the following equations:

For normal distribution

$$\text{FWHM} = 2\sigma (2 \ln 2)^{1/2} = 2.35 \sigma_D$$

μ_D = median

For lognormal distribution, σ_y is related to σ_D and μ_D by the following equations

$$\sigma_D = [\exp(\sigma_y^2) - 1].\exp(2\mu_y + \sigma_y^2)$$

$$\mu_y + \frac{1}{2}(\sigma_y)^2 = \ln(\mu_D)$$

These equations can be solved by successive approximations to find μ_y and σ_y .

The calculated μ and σ values are introduced in the models to calculate VSSA. For comparison, the model developed in this study and the model proposed by Roebben et al. 2014 are used. The VSSA values obtained by the two models, assuming spherical particles with a lognormal distribution, are presented in Table 9 together with the VSSA values obtained from BET surface areas.

The results in Table 9 show a good agreement between the VSSA values obtained by the BET surface area measurements and the VSSA values calculated from the TEM particle size distributions. Indeed, both models giving very similar results. This is because the particle size distributions are relatively narrow, and the particles have a sphere-like shape

Table 9 Comparison of TEM and adsorption to determine the VSSA. The Total VSSA is according to this study while the weight-averaged VSSA is according to Roebben et al.(2014).

Method	Sample	NM	NM	NM	NM	
		100	103	200	203	
ADS	VSSA from S_{BET} *	39	216	416	449	
	VSSA from S_{BET} (this study)	43.1	220.8	374	433	
	VSSA from S_w (this study)	23.3	76.6	356.4	237.6	
TEM	VSSA from median (total sample) **	47.6	285.7	270	400	
	Parameters of the normal distribution (total sample)	μ_D	126.6	21	22.2	15
		σ_D	46	8	10	4.7
	Parameters of the lognormal distribution (total sample)	μ_y	4.841	3.044	2.944	2.708
		σ_y	0.053	0.129	0.133	0.133
Total VSSA from this study	LN distribution	48.7	285	253	419	
Weight averaged VSSA according to Roebben et al 2014	LN distribution	47	298	277	374	

* Data from Nanogenotox 2013

** Data from Task 2.10. assuming that all particles have the median diameter

2.4.3.4 Application to a series of nano and non-nano samples

To cover a larger fraction of samples than those described in the previous chapters, some data from the Nanogenotox project, a series of industrial pigments, and on a multi-walled carbon nanotube were used.

The surface area measurements were performed by Currenta and the TEM data of pigments were provided by U. Hempelmann (Lanxess Deutschland GmbH). The data on CNT NC 7000 were provided by Nanocyl and the data on NM101 were taken from the Nanogenotox project. Overview of the data is presented in the Table 10.

Assuming the TEM data as the best possible estimate of the number particle size distribution, the results presented in Table 10 indicate that at least five samples (Fe₂O₃ Red 2 and Red 3, FeOOH Yel 1, NC7000 and NM101) could fall under nanomaterial definition; the median's value is less than 100 nm, and the percentage of particles under 100 nm is higher than 50%.

For the modelling approaches, we consider that the particle size distributions are almost of the log-normal type. This assumption is comforted by the particle size distributions obtained by TEM because they appear nearly normal on a logarithmic scale. The standard deviation of these distributions were calculated by the quartiles 25 and 75 (Q25 and Q75) according to the following equations:

$$\text{Mean} = [\ln(Q25) + \ln(Q75)] / 2$$

$$\text{Sigma } y = [\ln(Q75) - \text{mean}] / 0.67$$

The mean values of the aspect ratios indicating the shape factor of 6000, corresponding to nearly spherical particles, except for the multi-walled carbon nanotube.

The series of pigment's samples is rather interesting because they are either close to being or not to be nanomaterials, the percentage of particles with a size <100 nm being slightly below or slightly above 50 %. This is a good series to check the applicability of the VSSA approach with samples near the limit of the threshold.

The analysis of the measured VSSA obtained from adsorption data leads to the following conclusions:

- Due to high crystallization (as it appears on the TEM images), the pigments are considered non-porous, and the BET surface areas were used to calculate the VSSA. On the contrary, the NC 7000 and NM101 samples have a significant internal microporosity and hence, the external surface area (S_w) was used to calculate the VSSA.
- The five nanomaterials identified by TEM have a VSSA value based on BET and/or S_w surface areas higher than the threshold (60 m²/cm³ except for the CNT for which the threshold is 40 m²/cm³ due to fiber shape). On the other hand, two other samples considered as nanomaterials, indicating that the measured VSSA approach is indeed over protective.

In the modelling approach, the median and the standard deviation of the number distributions (as obtained by electron microscopy, Lanxess, and Currenta data) and

particle shape were introduced in the two models (the model developed in this study and Roebben et al. 2014.), to calculate the total VSSA. Log-normal distributions are used, and the integration covers sizes from 0.01 to 500 nm.

From the modelling it appears that:

- The percentage of particles with a size lower than 100 nm is in very good agreement. This means that the medians and standard deviations are representatives of the reality even if the measured distributions are not exactly of the lognormal shape.
- As the particle size distributions of these samples are relatively broad, the weight averaged VSSA values are systematically lower than the total VSSA values. As stated in the first part of this study, the difference between the models only appears for broad particle size distributions in which the large particles have a higher influence than the small ones.
- The total VSSA identifies that all the nanomaterials as nano, while the weight averaged VSSA identifies only one sample out of five (NC 7000) as nano. The total VSSA also identifies several pigments as nano confirming that the total VSSA values are over-protective, defining false identification of nanomaterials. Interestingly, the total VSSA values are very close the proximity to the threshold, confirming that these pigments are borderline cases.

Table 10 Adsorption, TEM and modelling data on a series of nano- and non-nano-materials. The density used to calculate the VSSA: for TiO₂ rutile, iron oxides pigment and CNT, values are taken from OECD database (OECD 2013) as reasonable proxies. The S_w values are measured in this study. The data highlighted in grey indicate that the samples could be considered as nanomaterials. Data highlighted in pink indicate nanomaterials not recognised as nano.

		Adsorption data			TEM data (Ferret diameter)					Modelling data			
Samples	Density g/cm ³	BET m ² /g	Sw m ² /g	VSSA m ² /cm ³	μD nm	σy	Shape	Aspect ratio	% particles <100 nm	Shape factor	VSSA m ² /cm ³	VSSA m ² /cm ³	% particles <100 nm
Cr2O3 pigment	5.22	5.5	-	28.7	107	0.527	platelet	1.6	44.1	6000	64	30	44.9
Fe3O4 Black 1	5.2	8.2	-	42.6	123	0.799	rhomb o	1.5	40.9	6000	66.4	21.3	39.8
Fe3O4 Black 2	5.2	7.1	-	36.9	195	0.485	rhomb o	1.2	13.3	6000	34.4	20.8	8.4
Fe3O4 Black 3	5.2	7.3	-	38	106	0.684	rhomb o	1.4	46.9	6000	71.2	24.5	46.6
Fe2O3 Red 1	5.22	13.3	-	69.4	104	0.672	rhomb o	1.4	47.2	6000	72.0	25.0	47.6
Fe2O3 Red 2	5.22	14.8	-	77.3	82	0.463	rhomb o	1.5	66.1	6000	81.4	43.0	66.6
Fe2O3 Red 3	5.22	12.2	-	63.7	84	0.410	rhomb o	1.5	65	6000	76.6	46.9	66.6
FeOOH Yel 1	4.25	14.2	-	60.4	80	0.456	rod	2.5	67.4	6000	83.2	44.7	68.85
FeOOH Yel 2	4.25	16.8	-	71.4	105	0.617	rod	2.1	46.1	6000	68.9	26.5	46.8
FeOOH Yel 3	4.25	13.9	-	59.1	103	0.565	rod	2.0	47.8	6000	68.3	28.9	47.9
NC 7000 CNT	2.05	270.7	145	297.3	9	0.453	fibre	>100	100	4000	404	352	100
TiO2 NM-101	4.23	316.9	56.6	239	22.6	0.879	rhomb o	1.52	95	6000	388.7	45.5	95.5
											This study	Roebben	

- The NC7000 sample is a multiwall carbon nanotube. The VSSA value calculated by the external surface area S_w , is in good agreement with the experimental data.
- The NM101 sample is a coated TiO₂ containing porous particles with a total surface area of 316.9 m²/g and an external surface area $S_w = 145$ m²/g (see Figure 14 hereafter). However, the external surface of the particles is irregular due to the coating. This coating generates a microporosity whose surface, appearing in the low-pressure region of the t-plot, is measured to be 88.4 m²/g. This implies that the surface area corresponding to the particle size is $145 - 88.4 = 56.6$ m²/g. This value is used to assess the VSSA because it corresponds to the size of the particle, as confirmed by TEM. Hence, the distribution is particularly broad ($\sigma_y = 0.879$), only the total VSSA identifies the sample as nano, the weight averaged VSSA being very low.

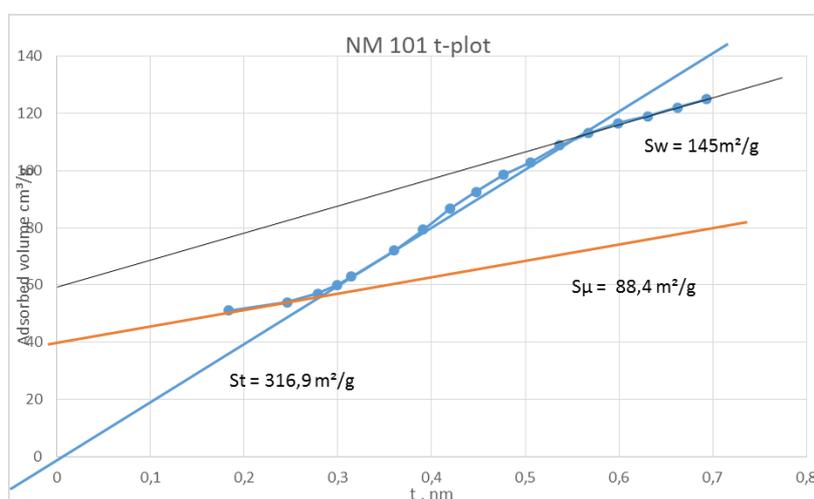


Figure 14 t-plot corresponding to the adsorption isotherm obtained for the sample NM101. From this plot, one can derive the total surface area S_t , the external surface S_w , and the surface area due to micro-porosity S_μ , generated by the coating.

2.4.3.5 Results obtained during the cooperation NanoReg and NanoDefine

A similar comparison between the experimental and theoretical values of the VSSA and the external specific surface areas was carried out during a cooperation between NanoReg and NanoDefine. The electron microscopy distributions and images as well as the low pressure part of the nitrogen adsorption isotherms were provided by the NanoDefine team. These data were used by NanoReg (Envicat) to assess the external specific surface area and to calculate the VSSA values from adsorption data and, by modelling from the electron microscopy data. The same type of distribution parameters and the same shape factors were of course used for both models.

This study shows that both models provide results in good agreement with the experimental data except for one sample characterised by a broad particle size distribution. For this

sample, the weight averaged VSSA is much lower value than the experimental VSSA, confirming that this model gives too low values for broad distributions.

Table 11 VSSA and External surface areas calculations by the two models compared to experimental values for the list of NanoDefine samples.

Material code	Density	VSSA m ² /cm ³			External Surface area m ² /g		
		ENVI model	JRC model	measured	ENVI model	JRC model	measured
381	4.28	11,4	11.1	9.84	2,65	2,6	2,3
382	2.05	347,6	310.6	315.7	169,3	151,5	154
383	5.12	50,7	48.1	46.6	9,8	9,4	9,1
384	2.657	27,9	27.6	16.5	10,1	10,4	6,2
385	2.61	37,6	35.7	40.5	14,1	13,7	15,5
386	1.5	28,3	27.8	26.1	18,8	18.5	17,4
387	4.01	175,3	168	151.6	43,7	41.9	37,8
388	3.99	30,9	24.7	31.1	7,7	6.2	7,8
<u>11</u>	<u>2.07</u>	<u>63,3</u>	<u>18,5</u>	<u>60.4</u>	<u>30,5</u>	<u>8.9</u>	<u>29,2</u>

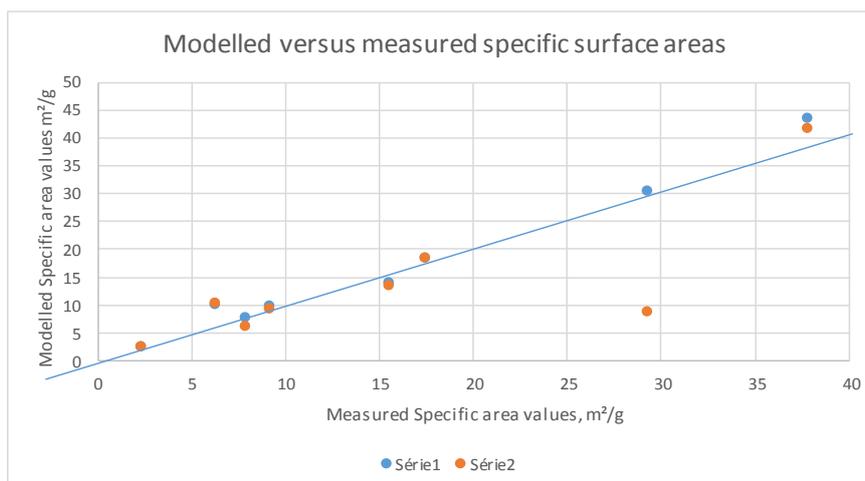


Figure 15 Comparison of modelled and measured VSSA for the NanoDefine list of samples. Series 1 (in blue): this study model, total VSSA. Series 2 (in orange): Roebben et al. model: weight averaged VSSA. The blue line represents the perfect match.

Another example considers a mixture of two BaSO₄ samples, one nano and one non-nano (material code 387 and 381 of the NanoDefine list) characterised by a median size of 20 and 260 nm respectively; their measured and by lognormal modelled particle size distributions are presented hereafter.

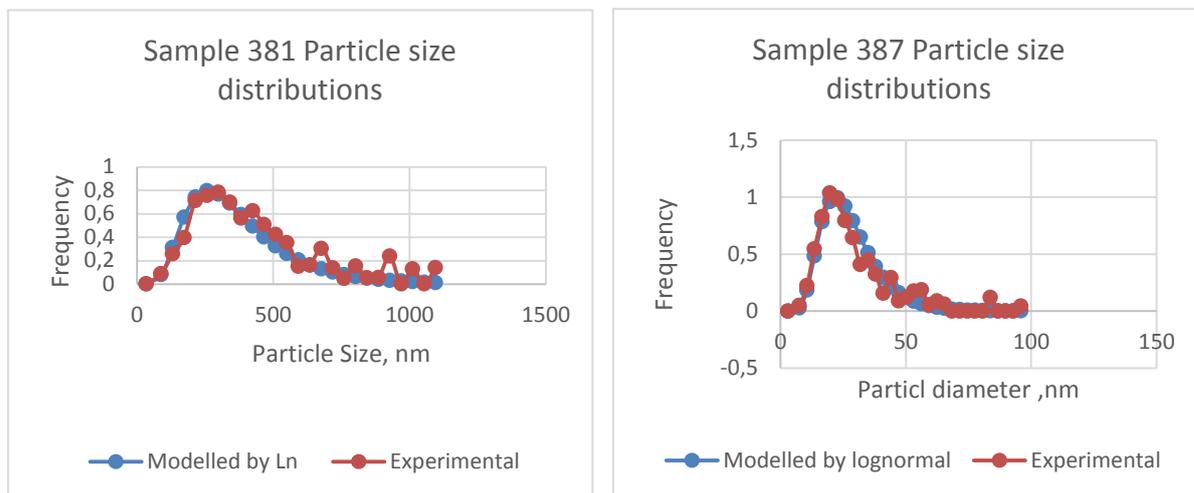


Figure 16 Experimental and log-normal particle size distributions of the two BaSO₄ samples constituents of the mixtures

The mixture contains 9 weight % of sample 387 and 91 weight % of sample 381, in order to obtain a bimodal distribution. This corresponds to a mixture containing about 97 number % of sample 387 and 3 number % of sample 381. Consequently this mixture is clearly a nanomaterial according to the EU definition.

Three independent BET measurements were performed on the mixture by two different labs and resulted in a mean VSSA of 23 m²/cm³ with a standard deviation of 3.3 m²/cm³. The sample is considered as non-nano confirming that the VSSA criterion is not applicable to bimodal particle size distributions.

In order to compare the two modelling approaches, both the total and the weight averaged VSSA are calculated for this bimodal distribution and the results are presented hereafter:

- The weight averaged VSSA value (24.3 m²/cm³) is much lower than the 60 m²/cm³ threshold confirming the experimental VSSA value and the fact that both experimental and weight averaged VSSA values cannot identify the mixture as nanomaterial.
- The total VSSA value (310.8 m²/cm³) of the mixture identifies it as nanomaterial but is much higher than the experimental VSSA value.

The consequences of this situation are the following:

- The experimental VSSA cannot be used as criterion for identifying nanomaterials characterised by a bimodal particle size distribution, because the specific surface areas should be combined on a weight to weight basis while the EU definition of nanomaterials is considering the combination of number distributions.
- For the same reason, the weight averaged VSSA obtained by the JRC model is not able to identify nanomaterial characterised by a bimodal distribution.
- As previously said, for samples characterised by a bimodal particle size distribution, the total VSSA is partly applicable as criterion to identify bimodal nanomaterials at the condition that the median of the nano-part of the sample is lower than 50 nm.

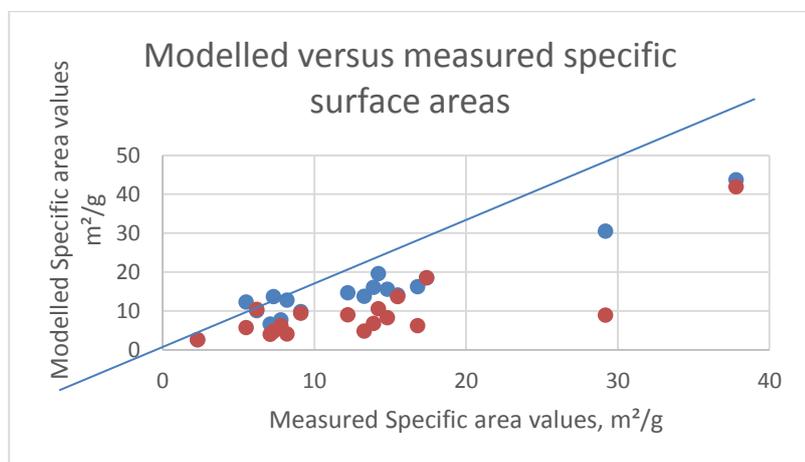


Figure 17 Comparison of experimental and modelled specific areas. Series 1 in blue: this study's model; series 2 in orange: Roebben et al. model. The blue line represents the perfect match.

2.4.3.6 Summary of experimental results

The two following diagrams show the comparison between experimental and modelled values of all the samples studied in the experimental part: the first one shows the external surface area and the second the corresponding VSSA. The blue line represents the perfect match.

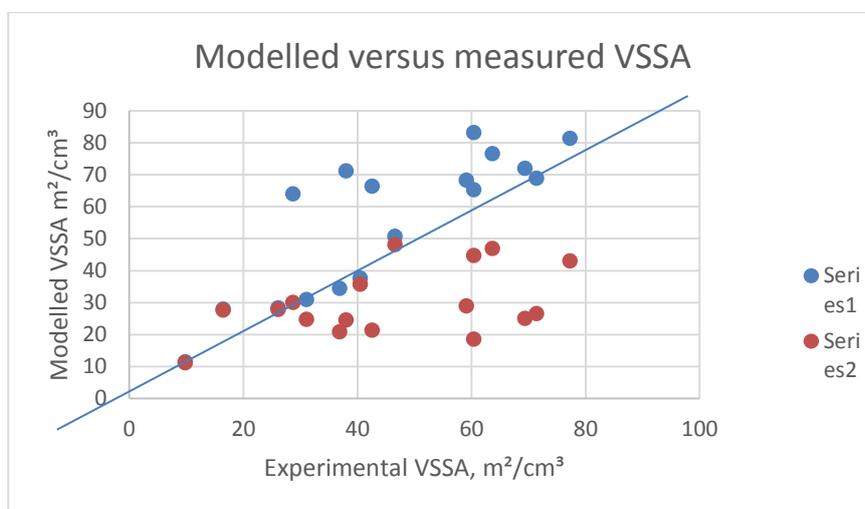


Figure 18 Comparison of experimental and modelled VSSA values. Series 1 in blue: total VSSA (this study model); series 2 in orange: weight averaged VSSA according to Roebben et al model. Blue line represents the perfect match.

2.4.4 Discussion

In the **theoretical part of the study**, a model was developed to calculate the **total VSSA** values corresponding to polydispersed particle size distributions. Total VSSA can be statistically qualified as the number weighted sum of the individual VSSA corresponding to each particle size present in the distribution with their frequency of appearance. It was assumed to be a reliable way of identifying nanomaterials at the condition to take into account the shape of the particles, their external surface instead of the BET surface area and the characteristics of the particle size distribution. The study shows that calculated total VSSA values are overprotective because they are leading to false identification of nanomaterials.

This model was challenged by a model developed by Roebben et al.2014 preferring the use of a **weight averaged VSSA** value. The shape of the particles is also considered as well as the polydispersity but not the porosity of the particles. They come to the conclusion that this model is under protective because nanomaterials characterised by a broad particle size distribution are not identified as nano and consequently they are leading to false negative identification of nanomaterials.

The **experimental part of this study** intends to compare experimental VSSA values to the VSSA via modelling, starting from the number particle size distributions parameters obtained by the analysis of TEM images.

Quality of adsorption data

In order to get reliable experimental results from adsorption data, several conditions should be respected. In the following paragraphs, the experimental results quality and reliability are discussed.

The reliability of the VSSA approach first depends on the quality of the adsorption data. As a first step, the reproducibility and repeatability of the surface areas obtained by applying the BET and the t-plot transformations of the nitrogen adsorption isotherms were studied in three laboratories.

The repeatability of the BET and the total surface area (S_t) values are quite satisfactory within each laboratory, while the reproducibility between laboratories strongly depends on the degassing conditions applied to the samples. For a comparable degassing conditions, an acceptable reproducibility is obtained i.e. about 7%. This corresponds to the generally accepted margin of error for adsorption data.

For porous, nanostructured or coated nanoparticles, the t-plot transformation should be used because only the external surface of the particle should be considered to calculate the VSSA. The internal porosity or the porosity created by the coating can be determined by analysing the low pressure area of the t-plot (low value of t). This requires to have not only good degassing conditions but also a sufficient number of experimental points in the low pressure region and to use the appropriate standard isotherm. In these conditions, the reliability of the t-plot analysis is very good.

To get reliable information on nanomaterials, the quality of adsorption data requires:

- a good degassing of the sample, under high vacuum, preferably in the adsorption apparatus for a significant number of hours, at room temperature to avoid modification of the sample
- to reach adsorption equilibrium at each experimental point
- to have enough number of experimental points in the low pressure region of the isotherm, in order to identify the internal porosity or the porosity generated by the coating
- ideally a complete adsorption isotherm or at least a sufficient number of experimental points to cover the relative pressure range from 0 up to 0.65.

If these conditions are respected, then the analysis of adsorption isotherms via the BET and the t-plot transformations will give reliable results.

2.4.5 Calculation of VSSA from adsorption data

As suggested by SCEHNIR, the VSSA can be calculated by dividing the surface area of the particles by their specific volume or skeletal density. The obtained value is compared to a threshold in order to identify the nano-character of the sample. The threshold value depends on the particle shape and requires **qualitative imaging** by transmission electron microscopy. Moreover, the VSSA method is valid only if the external surface of the particles is used, because this is the only surface linked to their size.

It was suggested to use the BET surface area but, this surface includes the internal porosity as well as the porosity generated by the coating. Consequently the use of the BET values to calculate the VSSA is only valid for non-porous and non-coated materials. If the VSSA calculated by using the BET surface area is lower than the threshold, then the sample is considered as non-nanomaterial. If the VSSA calculated by using the BET surface area is

higher than the threshold then, t-plot should be used to detect the presence of any internal porosity and to measure external surface of the particles. Finally, only the external surface is then used to calculate the VSSA to decide if the sample is nano- or non-nanomaterial.

This experimental procedure was used in this study and it appears that, if they are characterised by a **mono-modal particle size distribution**, all materials identified as nano because they have 50% of their number of particles below 100 nm (main EU criterion) are also identified as nanomaterials by this experimental VSSA approach. It means that for mono-modal particle size distributions, the experimental VSSA criterion is compatible with the 50% criterion based on the number particle size distribution.

2.4.6 The modelling approaches compared to experimental results

The VSSA values obtained by BET surface areas of non-porous samples or by the external surface areas (S_w) of porous samples, were compared to the VSSA calculated by both models i.e. the total VSSA or the weight averaged VSSA. These models are using the particle size distribution characteristics (median and standard deviation) obtained by analysis of the TEM images. All the results were summarised in **2.4.3.5** in the form of two diagrams.

For **narrow particle size distributions**, both models are giving similar results, in good agreement with experimental data if the particle shape is taken into account. Such an agreement confirms that the use of standard BET surface area is successful with no false negatives for non-porous samples. It further confirms that the t-plot evaluation of isotherm is a successful correction to resolve false positives that arise from samples containing micro-porosity or coatings of nm or sub-nm dimension.

For **broader particle size distributions**, the total VSSA values are higher than the experimental values and consequently it can identify all nanomaterials even if, in some cases, this total VSSA approach is, leading to identify false positive nano-materials. The total VSSA is then an overprotective criterion compared to the 50% of particles with a size lower than 100nm criterion applied to the number particle size distribution. On the contrary, the weight averaged VSSA values appear to be lower than the experimental values and consequently it is not able to identify most of the nanomaterials and is leading to many false negative cases. The weight averaged VSSA is then an under-protective criterion compared to the 50% of particles with a size lower than 100 nm criterion applied to the number particle size distribution.

The weight averaged VSSA values are most often below the experimental VSSA values when the particle size distribution is broadening, because, the volume contribution of larger particles increases rapidly with their size, leading to a reduction of the ratio overall surface to overall volume and consequently of the VSSA value. What is strange is the fact that the weight averaged VSSA was built to reproduce the experimental methodology and that it leads to VSSA values much lower than the experimental ones.

Interestingly, **on the Figure 18, the experimental VSSA values are either close to both modelled, data or, for broader particle size distribution, between the total and the**

weight averaged VSSA values and consequently the experimental VSSA can be used as criterion for identifying nanomaterials with a mono-modal particles size distribution.

2.5. Evaluation and conclusions

The above presentation made on the basis of the analysis of the nitrogen adsorption isotherms clearly shows that it is possible to identify the nano character of a material by using the **experimental VSSA criterion**.

To be able to do so, some conditions should be fulfilled:

- The particle size distribution is mono-modal
- The adsorption data should be of good quality as described before (effective degassing of the sample, equilibrium at each experimental point, sufficient number of experimental points to cover the relative pressure range from 0 up to 0.65).
- It is necessary to have an elementary knowledge of the material under test like its chemical nature, the presence of a coating and some structural data. In particular, a qualitative image by transmission electron microscopy is needed to define the particle shape.

If these conditions are respected, then the analysis of adsorption isotherms via the BET and the t-plot transformations will give reliable results and the following process should be followed:

- If the VSSA calculated by using the BET surface area is lower than the threshold, then the sample should be considered as non-nanomaterial.
- If the VSSA calculated by using the BET surface area is higher than the threshold then the t-plot should be used to detect the presence of an internal porosity or the presence of a coating and to estimate the external surface of the particles as illustrated several times in this paper.
- This external surface is then used to calculate the VSSA which is compared to the threshold to decide if the sample is nano- or non-nano- according to the EU definition.

This procedure was used in this paper and it appears that all nanomaterials were identified by this VSSA approach. To avoid the identification of false positive nano-materials, the following process should be followed:

- If the VSSA is lower than the threshold, then the material should be considered as non-nano.
- If the VSSA appears to be slightly higher (about 20%) than the threshold, it is necessary to determine the particle size distribution by TEM image analysis to decide the nano character of the material.
- If the VSSA is much higher than the threshold, the material should be considered as nano.

This confirms that the experimental VSSA criterion is a simple practical way to assess the “non-nano” character of a powder characterised by a mono-modal particle size distribution without using expensive sophisticated methods based on number particle size distribution

The two models developed to calculate the VSSA values starting from the number particle size distributions were discussed and their results compared to the experimental values.

The first model leading to total VSSA is based on the VSSA concept developed for monodispersed particles and is the number weighted sum of the individual VSSA corresponding to each particle size present with its own frequency in the distribution.

The second model leading to a weight averaged VSSA is based on the measurement method, dividing the total surface area of all the particles by their total volume. This corresponds to the inverse of the Sauter mean diameter.

In case of **mono-modal particle size distributions**, both models are giving similar results in good agreement to the experimental results, if the number particle size **distributions are relatively narrow**. But **when the particle size distribution is broadening** the total VSSA values are becoming higher than the experimental values while the weight averaged VSSA is are lower than the experimental ones. As the experimental VSSA values were demonstrated to be a good criterion to identify nanomaterials, the total VSSA values appear to be overprotective leading to false positive nanomaterials while the weight averaged VSSA values are under-protective and leading to false negative nanomaterials.

For **bimodal particle size distributions**,

- The experimental VSSA cannot be used as criterion for identifying nanomaterials, because the specific surface areas should be combined on a weight to weight basis while the EU definition of nanomaterials is considering the combination in number of particles.
- For the same reason, the weight averaged VSSA is not able to identify nanomaterial characterised by a bimodal distribution.
- The total VSSA is partly applicable as criterion to identify nanomaterials at the condition that the median of the nano-part of the sample is lower than 50 nm.

3. Deviations from the work plan

No deviation from the planned work.

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SCENIHR Scientific Basis for the Definition of the Term "nanomaterial" The SCENIHR approved this opinion by written procedure on 8 December 2010

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6 Annex 1: D 2.11: Standard Operating Procedure (SOP) for VSSA analysis of primary NM in air, powders and liquids and how to use it to identify Nanomaterials

6.1 Executive summary

One of the outcomes of NanoReg (Deliverable D2.11) is to describe the texture of nanomaterials by nitrogen adsorption isotherms in order to determine not only VSSA value but also to demonstrate the potential of adsorption isotherm for nanomaterials of different shape and size.

6.1.1 Quality of adsorption data

- The procedure for measuring the surface area by nitrogen adsorption isotherms is according to ISO (2006, 2007 and 2010) and IUPAC (1985). The most critical step in the measurement is the outgassing stage, i.e. to clear the adsorbent surface to any adsorbed molecules before the measurements.
- The outgassing process of the solid sample can be performed at room temperature, or at a higher temperature to promote desorption of strongly adsorbed species. The pre-treatment conditions must remain sufficiently mild to avoid any modification of the textural characteristics of the sample but severe enough to obtain a good surface clean-up. It is recommended to perform the pre-treatment in the cell used to carry out the adsorption. Whatever the temperature, the solid must be submitted to a minimum vacuum of 10^{-2} Nm⁻² i.e. 10 mPa during at least one hour. Such conditions are readily achieved with the aid of conventional vacuum equipment, usually a combination of a rotary and diffusion pump. In general, the lower the temperature, the longer the outgassing process should be.
- A larger the numbers of experimental points are always recommended to measure during the measurements. For nanomaterials and nanostructured materials, it is recommended to multiply the number of points in the low-pressure region of the isotherm.

As a consequence, to get appropriate information on **nanomaterials**, the quality of adsorption data requires

- a good degassing of the sample, under vacuum in the adsorption apparatus, during a few hours, at room temperature to avoid modification of the sample
- to reach adsorption equilibrium at each experimental point
- a large number of experimental points in the low pressure region of the isotherm in order to well identify the internal porosity of the particle or the porosity generated by a coating.
- Ideally, a complete adsorption isotherm or at least a sufficient number of experimental points to cover the relative pressure range from 0 up to 0.65 is needed.

Remark: This applies to powders or to liquid suspensions after a smooth drying step. For extremely small quantity of nanomaterial (i.e., micro grams), sorption isotherm may not

suitable. It is however possible to calculate the VSSA from particle size distribution obtained by electron microscopy.

6.1.2 VSSA calculation from adsorption data

If these experimental conditions are respected, the adsorption isotherms are considered as reliable and can be analysed via the BET and the t-plot transformations. It should be clear that the VSSA approach is valid only if the external surface of the particles is used, because this is the only surface linked to their size.

In general, BET method is used to measure the surface area but, this surface area includes the internal porosity of the particles as well as the porosity. **Consequently the use of the BET value to calculate the VSSA is only valid for non-porous and non-coated materials.**

For porous, nanostructured or coated nanoparticles, the t-plot transformation should be used because the internal porosity or the porosity created by the coating can be determined by analysing the very low pressure area of the t-plot (low value of t) at the condition to have a sufficient number of experimental points in this low pressure region and to use the appropriate standard isotherm as described by Lecloux (1979). See the full text to get these standard isotherms. The surface generated by these porosities should be subtracted from the total surface area to get the external surface linked to the size of the particles. Examples are given in the full-text.

The VSSA is obtained by dividing the external surface area of the particles by their specific volume and then compared to the threshold values to decide if the sample is nano- or non-nano- according to the EU definition. It should be pointed out that the threshold depends on the particle shape. The comparison is only possible if the shape of the particle was determined by a qualitative image obtained by transmission electron microscopy.

6.1.3 Identification of nanomaterials

If the VSSA calculated by using the BET surface area is lower than the threshold, then the sample should be considered as non-nanomaterial, while the BET surface area is higher than the threshold then the t-plot should be used to detect the presence of an internal porosity or the presence of a coating and to estimate the external surface of the particles. This external surface is then used to calculate the VSSA.

It seems that all nanomaterials were identified by VSSA approach and the results obtained are quite comparable to the information obtained by electron microscopy, even if, in some cases the VSSA approach is overprotective, leading to identify false positive nanomaterials.

As VSSA approach is overprotective, the three following cases are considered:

- If the VSSA corresponding to the external surface area of the particles is lower than the threshold, then the material should be considered as non-nano.
- If the VSSA appears to be slightly higher (about 20%) than the threshold, it is necessary to determine the particle size distribution by TEM image analysis to decide the nano character of the material.

- If the VSSA is much higher than the threshold, the material should be considered as nano.

The relative good agreement between these experimental VSSA values and the calculated VSSA values on the basis of the particle size distributions obtained by TEM image analysis provides confidence in both approaches.

This confirms that the VSSA criterion is a simple practical way to assess the “non-nano” character of a powder without using expensive sophisticated methods based on number particle size distribution

6.2 PART I: Basic information and sample preparation

6.2.1 Introduction

The physical-chemical characterisation of materials is very important to correctly assess their toxicological and eco-toxicological properties.

The main physical features of a material are:

- Its structure, i.e. the nature and the geometrical distribution of atoms or ions in the material and in particular on its surface
- Its texture, i.e. the detailed geometry of the void space in the particles from the inter-granular voids in the agglomerates down to the pore size distribution at the finest level of resolution, from the shape of the particles and their internal surface area down to the pore shapes and the extent of the accessible internal surface.

The aim of this task is to propose guidelines and methods for a systematic investigation of textural properties of a material with an aim of identifying their nano character.

The two principal means to get a reasonably good description of the texture of solid materials are physical adsorption isotherm analysis and mercury porosimetry. Combining the data with particle size analysis and crystallographic studies, one could get textural properties of a material..

6.2.2 Definition of parameters to describe solid texture

It is impossible to give an exact and detailed description of a porous solid at an atomic level, different properties are generally used [1]:

- *The specific surface area* is a measure of the accessible surface area per unit mass of solid; and it is a sum of the internal surface area associated with pores and external surface area. If the surface area is expressed per unit volume it is called volume specific surface area (VSSA), but it implies to know the density of the solid.
- *The specific porosity* refers to the accessible pore void space in the particles per unit mass of solid; it eventually includes the inter-granular void space in agglomerates and aggregates
- *The pore shape* is generally difficult to describe with a rather good precision. It is the reason why the pores are usually classified into groups corresponding to types of pore shapes: cylindrical, ink-bottle and slit-shaped pores. But in practice, other pores of different shapes may be present in a solid and interconnections. However, in the case of zeolite, the pore shape can also be completely determined by the crystal structure of the

solid.

- *the pore size distribution* is the distribution of the pore volume (or pore area) versus the pore size. It is an important factor for the kinetic behaviour of porous solids in their applications as catalysts, membranes or filters for example. But the computation of such a distribution always involves some assumptions that we must always bear in mind in the everyday practice. In general, due to the experimental methods used (adsorption of fluid, mercury porosimetry), the pore size distribution does not give the exact volume (or area) of the pores at a given pore size. The pore size distribution thus depends on the shape of the pores present in the solid.
- *the mean pore size* corresponds to the mean value of the pore size distribution. It can be calculated by dividing the specific porosity by the specific surface area, the result being multiplied by a factor depending on the pore shape. It is therefore expedient to classify pores according to their mean sizes:
 - (i) pores with widths exceeding about 50 nm are called macropores;
 - (ii) pores with widths not exceeding about 2nm are called micropores;
 - (iii) pores of intermediate size, i.e., 2 -50nm are called mesopores.

Though, the limits are accepted at international level [16, 17], to some extent the limits are arbitrary since the pore filling mechanisms are dependent on the pore shape and are influenced by the properties of the adsorptive and the adsorbent adsorptive interactions [2, 3].

It has to be pointed out that the micropore range is further subdivided into pores smaller than about 0.7 nm (ultramicropores) and pores in the range from 0.7 – 2 nm (supermicropores). The pore size is generally specified as the internal pore width (for slit-like pores) or pore radius/diameter (for cylindrical and spherical pores) [9].

- *the particle size distribution* is the distribution of the mass, surface or number of particles as a function of their size. Generally the particles are supposed to be "spheroidal" but in some cases a shape-factor must be taken into account, in particular for sheet - or fibre - like materials. A mean particle size is very often used: it generally corresponds to the mean value of the particle size distribution.
- *the shapes and the sizes of agglomerates of elementary particles* in larger objects like granules, pellets or extrudates are rather well defined and characterized by simple geometrical parameters.

6.2.3 Experimental remarks

Before going in to details of experimental techniques, it is worth emphasizing most important points for a correct determination of the porous texture of solids.

6.2.3.1 Choice of Adsorptive

Only physical adsorption is considered here i.e. adsorption between the solid, called *adsorbent*, and the fluid, called *adsorbate*, are intermolecular forces of the van der Waals type. These forces are of the same kind as those responsible for deviation from ideality of the real gases and the condensation of vapors; they do not significantly change the

electronic orbital patterns of the species involved. In this case the adsorption phenomenon is strongly dependent on the physical properties of the solid and in particular on its porous texture. But if the adsorbent-adsorbate interactions involve valence forces, strong hydrogen bonds or charge transfer complexes, the adsorption phenomenon is no longer representative of the sole physical properties of the solid and consequently can no longer be used to determine the texture of the adsorbent.

This fundamental remark implies that the adsorbate-adsorbent interactions must be kept at a level such that the physical properties of the solid are shown through adsorption but are not masked by its chemical behaviour.

Consequently,

- (i) the adsorptive must be as chemically inert as possible
- (ii) vapours must be preferred to liquids or gases as adsorptive
- (iii) adsorption temperature and pressure will usually be low.

Furthermore, if a high level of resolution in the pore structure is needed, the adsorptive molecules (or atoms) must be small enough so as to enter the whole pore space. In these conditions, the most commonly used adsorptives are nitrogen, argon or krypton.

As pure nitrogen is readily available and less expensive than argon and krypton, nearly all the textural studies of solids are carried out on the basis of nitrogen adsorption isotherms.

6.2.3.2 Pre-treatment of the Adsorbent

In general, the adsorbent surface is cleared out of any adsorbed molecules - by out gassing - before the measurements.. The out gassing process of the solid sample can be performed at room temperature, or at a higher temperature to promote desorption of strongly adsorbed species. It is important to point out that the out gassing temperature must be kept below the temperature of the last thermal treatment to which the solid has been processed; otherwise the sample texture may be changed. **At a moderate temperatures, it is recommend to apply the degassing conditions at a vacuum of 10^{-2} Nm⁻² i.e. 10 mPa for at least one hour.** Such conditions are readily achieved with the aid of conventional vacuum equipment, usually a combination of a rotary and diffusion pump. In general, the lower the temperature, the higher the out gassing process.

The pre-treatment conditions must remain sufficiently mild to avoid any modification of the textural characteristics of the sample but severe enough to obtain a good surface clean-up. It is recommended to perform the pre-treatment in the cell used to carry out the adsorption.

Particular attention may be required for solid particles collected from a suspension. It is recommended to dryout the solvent smoothly to avoid any process related discrepancy. During the drying, the individual particles can form agglomerates in which the particles are not chemically bounded. It may not influence their surface area, but it rather changes the inter-particulate volume. But if the drying conditions are too severe (for example if a high drying temperature is used), the particles may form aggregates with a modification of their surface area as-well. It is then important to dry the suspension at low temperature under vacuum to avoid the formation of aggregates.

6.2.3.3 Adsorption Isotherm Determination

The adsorption isotherm relates to the amount of substance adsorbed at an equilibrium to adsorptive pressure in the gas phase [1, 2], at a given temperature. The adsorbed amount is given by a number of moles or by the corresponding volume at STP conditions. As the temperature of adsorption is usually lower than the critical temperature of the adsorptive, the adsorbed amount is generally given as a function of the relative pressure, i.e. the pressure in the gas phase, p , divided by the saturation pressure, p_s at the same temperature. In these conditions the adsorption isotherm can be represented for a given gas-solid pair by:

$$v = f(p / p_s)_T \quad (1)$$

where v is the amount adsorbed, p / p_s the relative pressure and T the temperature. Whether the v values are determined for increasing the pressure (from $p/p_s \sim 0$ up to $p/p_s = 1$) or decreasing the pressure (from $p/p_s = 1$ down to $p/p_s \sim 0$), the adsorption branch or desorption branch of the isotherm is obtained. In general, the two branches of the isotherm do not coincide with each other: there is a hysteresis loop, characteristic of the "mean shape" of the pores present in the solid.

To obtain an accurate determination of the adsorption-desorption isotherms two different methods can be used:

- the gravimetric method where the weight variations of the solid sample are determined for increasing or decreasing the vapour pressure. This method is very accurate but it calls for a very sensitive and sophisticated microbalance
- the volumetric method where the volume of adsorbed species is determined as a function of the pressure. This method is in principle less accurate than the gravimetric method but it is extensively used because only a rather simple glass apparatus is needed

Whatever the experimental method used, the reliability of the results will depend on the knowledge of the actual working temperature. If nitrogen (or argon) is the adsorptive, the adsorption isotherms are determined at liquid nitrogen (or argon) temperature, by using a Dewar containing the corresponding liquid.

It is essential to keep the **temperature** constant throughout the experiment:

- The sample bulb must be immersed to a depth of at least 5 cm below the liquid nitrogen (or argon) level.
- The liquid bath must be kept in the boiling state, for example by bubbling the corresponding gas through the liquid.
- The level of liquid nitrogen in the bath must be kept constant to within a few millimetres, preferably by means of an automatic device.

A slight variation of the boiling temperature of the liquid nitrogen (or argon) bath can be observed due to the slow but regular dissolution of the air components in the liquid bath and, in a lesser extent, to modifications of the atmospheric pressure. **These small temperature variations can strongly affect the value of the saturation pressure p_s** , and, consequently the whole relative pressure scale of the isotherm.

In practice, the **saturation pressure** must be measured at the temperature of the liquid bath containing the sample cell. A simple way of doing this is to use a gas manometer filled with the adsorptive used for the adsorption experiment and to keep it in the liquid bath

containing the sample cell. In some cases, a precise knowledge of the atmospheric pressure is needed.

The temperature of the solid sample is supposed to be the same as the liquid bath temperature. However, Nicolaon [4, 5] showed that temperature gradients may exist between the sample and the liquid bath **when the gravimetric method** is used. This is due to the fact that there is no direct contact between the liquid bath and the basket of the microbalance containing the solid and, consequently an appreciable time may be required to reach the equilibrium.

In the application of a **volumetric technique** involving a dosing procedure it must be kept in mind that any errors in the measured doses of gas are cumulative and that the amount remaining unadsorbed in the dead space becomes increasingly important as the pressure increases. This is why the dead spaces should be minimised and parts of the apparatus containing appreciable volumes of gas must be thermostatted, preferably to $\pm 0.1^\circ\text{C}$. If possible the whole apparatus should be maintained at reasonably constant temperature. The nitrogen (or argon) used as adsorptive must be of **purity** not less than 99.9%.

In the volumetric measurements, a known quantity of gas is usually admitted to a confined volume containing the adsorbent, maintained at constant temperature. As adsorption takes place, the pressure in the confined volume falls until equilibrium is established. The amount of gas adsorbed at the equilibrium pressure is given as the difference between the amount of gas admitted and the amount of gas required to fill the space around the adsorbent, i.e. the dead space, at the equilibrium pressure. The adsorption isotherm is constructed point-by-point by the admission to the adsorbent of successive charges of gas with the aid of a volumetric dosing technique and application of the gas laws. It is important that the process will be carried out in such a way that **equilibrium is reached** after each dose of gas introduced in the apparatus. The volume of the dead space must, of course, be known accurately: it is generally obtained by the admission of a non-adsorbable gas like helium in the apparatus containing the sample.

Whether the adsorption-desorption isotherms are determined by a gravimetric or a volumetric method, it is worth pointing out the following remarks:

- **the adsorbent pre-treatment** (handling in an eventually controlled atmosphere, thermal treatment, outgassing, ...) must be adapted to each particular case and never modify the porous texture of the solid. When **nanomaterials** are examined, it is particularly important to out-gas the adsorbent under vacuum as recommended, in order to clear the very small pores and the voids between the particles.
- **the actual saturation pressure** of the adsorptive at the temperature of measurement must be known with very good precision., Its value is indeed of importance not only for the accurate determination of the isotherm but also for its correct analysis.
- the larger **the number of experimental points** used to define the sorption isotherm, the more efficient its analysis will be and, consequently the more detailed the description of the textural properties of the adsorbent. For applying the BET or the Dubinin model (see Part II hereafter) at least 6 to 10 experimental points well distributed between $p/p_s = 0$ and $p/p_s = 0.35$ are needed. The use of the t -, the α_s - or

the n-method needs about 20 experimental points in the relative pressure range between 0 and 0.65. Finally, the BdB method for calculating the pore size distribution also requires at least 20 experimental points to define each branch of the isotherm. To multiply the number of points in the low pressure region is particularly important for **nanomaterials and nanostructured materials**. All these methods are described in the second part of this paper.

The above remarks must be taken into account to appreciate to what extent an experimental adsorption-desorption isotherm is worth being used to characterize the porous texture of the adsorbent. The validity of the porous texture derived from sorption isotherm depends on the quality of the experimental determination.

6.3 PART II: Analysis of the isotherms

6.3.1 Classifications of Isotherms According to Their Shape or Their Hysteresis Loop

In 1940, Brunauer et al. [6] proposed to classify the physical adsorption isotherms in five different groups numbered from I to V. The classification relates the shape of the isotherms to both the mean pore size of the adsorbent and the intensity of adsorbate-adsorbent interactions [7]. The five types of adsorption isotherm are schematically represented on Figure 19.

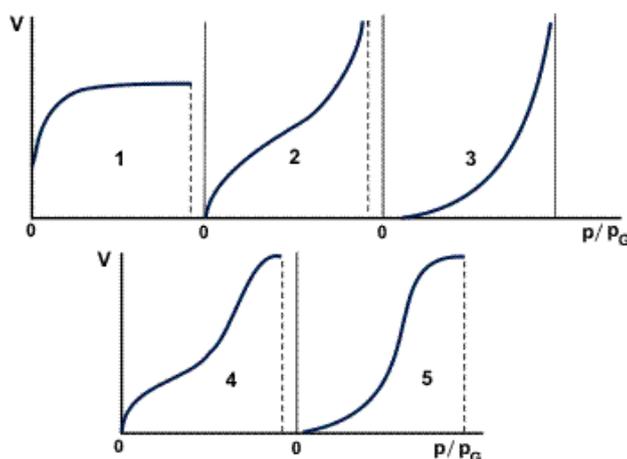


Figure 19 Classification of isotherms according to their shape

- *Isotherms of type I* are characteristic of microporous adsorbents
- *Isotherms of types II and III* are observed for macroporous adsorbent. Type II isotherms frequently occur. On the contrary type III isotherms are rather unusual and correspond to very weak adsorbate-adsorbent interactions
- *Isotherms of types IV and V* are obtained for mesoporous adsorbents. Type IV isotherms are widespread whereas type V isotherms (which correspond to very weak adsorbate-adsorbent interactions) are seldom encountered.

In everyday practice, the shape of the isotherm usually gives a rather good idea of the mean size of the pores present in the solid. Sometimes however, an isotherm cannot be related to one definite group of this classification because different types of pores are present in the adsorbent. These "mixed" isotherms are also indicative of the general porosity of the solid.

Another easy way to get information on the porous texture of the adsorbent is to look at the shape of the **hysteresis loop**. The presence of a hysteresis loop is always observed with isotherms of types *IV* and *V* and sometimes with isotherms of types *II* and *III*. A classification of the hysteresis loops has been proposed for the first time by de Boer [8] and four categories of hysteresis loops were adopted by the IUPAC [2] and were related to the general shape of the pores present in the solid, as illustrated in Figure 20.

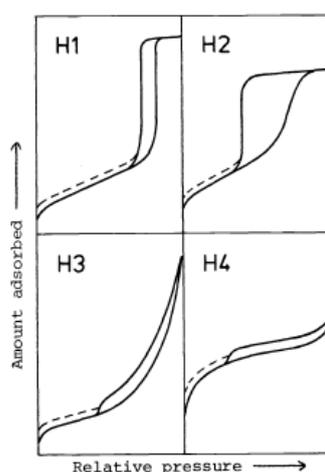


Figure 20 Type of hysteresis loops according to IUPAC [2]

- Type H1 hysteresis had been associated with "cylinder shaped" pores of rather constant cross section or with narrow pore size distribution.
- Type H2 hysteresis corresponds to a wide pore size distribution or to pores with narrow necks and wide bodies (often referred to as 'ink bottle' pores)
- Type H3 hysteresis, which does not exhibit any limiting adsorption at high relative pressure, is observed with aggregates of plate-like particles giving rise to slit-shaped pores.
- Type H4 hysteresis appears to be associated with narrow slit-like pores, but in this case the Type I isotherm character is indicative of microporosity.

In practice, the hysteresis loop shape may appear rather different from the ideal curves presented in Figure 19, but still the classification is useful in predicting the pore shape and other associated features of the porous solid. The main reason for these differences is the existence of a more or less broad pore size distribution, whereas the models used are based on ideal solids where all the pores have the same size. In general **the broader the pore size distribution, the wider the hysteresis loop**. Furthermore, "mixed" hysteresis loops may often be observed if different pore shapes are present in the same solid. The

absence of hysteresis may indicate either that the solid is microporous (type I isotherm) or that the pores are nearly perfect cylinders closed at one end, or that the solid is non porous.

A general inspection of the isotherm shape coupled with the analysis of the shape and the width of the hysteresis loop can indeed give the textural characteristics of a solid.

6.3.2 The BET model

Since the publication, in 1938, by Brunauer, Emmett and Teller [10], a famous model for physical adsorption of vapours on solids, the BET-theory and its use as a tool for determining the specific surface area of solids [7, 9, 11]. The limitations and the range of applicability of the BET-model have been critically discussed by several authors. In this respect, the book of Gregg and Sing [7] and the review paper of Nicolaon [4] are particularly worth reading. Apart from the critics, the applicability of the BET theory is still widely used and is accepted as a standard method of determining the surface area of any powder solid.

6.3.2.1 The Hypothesis of the BET Theory

The BET theory is based on various hypotheses, which is important for a good understanding of the model, limitation and its correct use in the textural analysis of solids.

The main assumptions of this theory can be summarized as follows:

- the adsorption is supposed to be localized on well defined sites, and the sites have the same energy (homogeneous surface), and each of them can only accommodate one adsorbate molecule
- a multilayer adsorption is supposed to occur even at very low pressure. The adsorbed molecules in the first layer acting as adsorption sites for the molecules of the second layer and so on; there is no lateral interaction between adsorbed molecules
- an adsorption-desorption equilibrium is supposed to be effective between molecules reaching and leaving the solid surface; the desorption is an activated process, the activation energy being E_{ADS} for the molecules adsorbed in the first layer and E_{COND} for the molecules adsorbed in the other layers. The E_{ADS} value is taken as the differential heat of adsorption of adsorbate molecules on the solid surface. The E_{COND} value corresponds to the heat of condensation of the adsorbate at the adsorption temperature. Except for the first layer, the adsorbate molecules are thus supposed to be as in the liquid state

6.3.2.2 The BET equation

The physical and mathematical treatment of these hypothesis leads to the following equation of an isotherm

$$v = \frac{v_m c p}{(p_0 - p) \{1 + (c - 1)(p / p_0)\}} \quad (1)$$

where

- v is the adsorbed volume,
- v_m is the volume of adsorbate just sufficient to cover (with a complete monolayer of molecules in close packed array) the surface developed by the unit

mass of adsorbent;

- c is a constant varying with the adsorbent-adsorbate interactions; it is related to the differential heat of adsorption E_{ADS} and to the heat of condensation E_{COND} by the following relation

$$c \approx e^{\frac{E_{ADS} - E_{COND}}{RT}} \quad E_{ADS} \gg E_{COND} \quad (2)$$

- p is the pressure corresponding to the adsorbed volume
- p_0 is the saturation pressure at the temperature of measurement

With this relation, called the "BET equation", it is possible to describe five different types of adsorption isotherms encountered in practice and represented in Figure 19, simply by using the appropriate values of c and v_m [7, 10, 11]. However the theoretical and experimental isotherms coincide only over a limited pressure range, which is a limitation from the assumptions the BET-theory is based. This theory indeed takes into account neither the heterogeneity of the solid surface, which mainly affects the low pressure part of the isotherm, nor the lateral interactions between adsorbed molecules which become more and more important as the pressure increases. Consequently, the BET equation is normally able to correctly describe a physical adsorption isotherm only in the relative pressure range between 0.05 and 0.35. These limits are indicative [7] for they can vary slightly from one adsorbent-adsorbate pair to another.

The BET-equation is more conveniently written in the following linear form

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{p}{p_0} \quad (3)$$

If we pose the relative pressure $p/p_0 = x$, then by plotting $y = x / v(1-x)$ as a function of x, for x varying between 0.05 and 0.35 a straight line

$$y = ax + b$$

should be obtained if the BET-model is valid. From this so-called BET-plot it is easy to obtain, by graphical or numerical methods, the values of a and b from which the values of the two parameters of the BET-equation, c and v_m can be derived:

$$c = a/b + 1$$

$$v_m = 1 / (a+b)$$

The c-value is characteristic of the intensity of the adsorbate adsorbent interactions.

As the c parameter is related to the differential heat of adsorption, the stronger the adsorbate-adsorbent interactions, the higher the c-value, whatever the type of porosity present in the solid.

As shown in Figure 21, the c-value greatly affects the shape of the isotherm in the low pressure region ($p/p_0 < 0.2$), whatever the v_m value [4, 7].

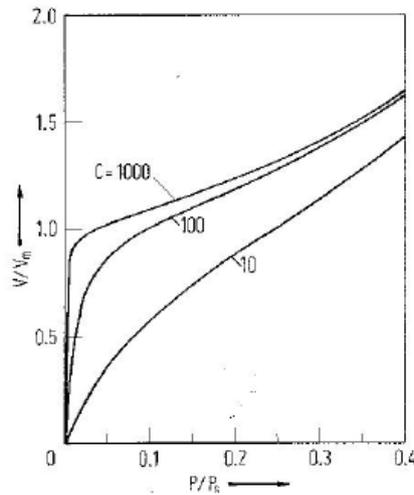


Figure 21 Influence of the c-value on the shape of adsorption isotherm in the BET-model.

6.3.2.3 Specific surface area according to the BET-model

The v_m -value is directly proportional to the specific surface area of the adsorbent, because v_m is, by definition, the amount of adsorbate just sufficient to cover with a complete monolayer the whole surface developed by the unit mass of adsorbent. The specific surface area of the solid is thus equal to the area occupied by one adsorbate molecule multiplied by the number of adsorbate molecules contained in v_m so that

$$S_{\text{BET}} = a_m \cdot v_m \cdot N_A / V_m \quad (4)$$

where

- S_{BET} is the specific surface area according to the BET-model
- v_m is the monolayer capacity of the unit mass of solid
- N_A is the Avogadro constant
- V_m is the molar volume of the adsorbate
- a_m is the part of surface occupied by one molecule of adsorbate in a closed layer.

In the case of nitrogen adsorption at liquid nitrogen temperature (77 K) the most widely admitted [2, 7] and used value of the area occupied by a nitrogen molecule is

$$a_m(\text{N}_2) = 16.2 \times 10^{-20} \text{ m}^2$$

In these conditions, if N_A and V_m are taken respectively equal to $6.025 \times 10^{23} \text{ mole}^{-1}$ and $22.414 \times 10^{-3} \text{ m}^3 \cdot \text{mole}^{-1}$, the specific surface area of the solid (expressed in m^2/kg of solid) is given by

$$S_{\text{BET}} = 4.37 \times 10^6 v_m \quad (5)$$

v_m being the monolayer capacity expressed in m^3 STP of N_2/kg of solid.

If other adsorbates than nitrogen are used, it is rarely possible to assign a fixed value to the

molecular surface area a_m of a given adsorptive. In general a range of value is given for each adsorptive [7] but, from their comprehensive review of the literature, McClellan and Harnsberger [12] "recommend" the following values of a_m expressed in 10^{-20} m^2

Ar at 77 K: 13.8
Kr at 77 K: 20.2

However, great caution should be exercised while using these values, because the molecular surface area of an adsorbate depends somewhat on the nature of the adsorbent. But for nitrogen, the molecular area of $16.2 \times 10^{-20} \text{ m}^2$ is considered as a reference value.

6.3.2.4 Limitations of the BET-model

Although the BET theory is based on a very simple model and can only describe a rather small part of adsorption isotherms, it works quite satisfactorily for determining the specific surface area of a range of solids. In fact, for non porous, macroporous and mesoporous solids, S_{BET} obtained from nitrogen adsorption isotherm must be considered in the present state of our knowledge as the best measure of the specific surface area. However the S_{BET} value can be determined without any limitations and with a good accuracy only from isotherms of types II and IV (cf. Figure 19) which fortunately are the most common isotherms.

In principle, the BET equation can also describe the other types of adsorption isotherm but the specific surface area determination is subjected to drastic limitations. The isotherms of type III and V typical of very weak adsorbent-adsorbate interactions, it is impossible to determine with a sufficient accuracy the S_{BET} value for two main reasons:

- the value of the c constant in the BET equation is nearly equal to one and in this condition, it has been shown [4, 7] that for mathematical reasons the v_m value is very sensitive to the slightest variation of c
- the adsorbed amounts are generally very small so that the determination of the interesting part of the isotherm may not be very accurate [12].

These two effects have such a cumulative unfavourable influence on the accuracy of S_{BET} determination that it is not worth calculating a specific surface area from isotherms of type III or V. The only possibility to get round this difficulty is to change the nature of the adsorbate in order to increase its interaction with the adsorbent and thus to obtain an isotherm of type II or IV.

On the other hand, with isotherms of type I, the calculation of S_{BET} can be made with a very good mathematical accuracy but the physical meaning of the value obtained in this way is a much debated question because Type I isotherms are characteristic of microporous solids in which the pore sizes are of the same order of magnitude as the size of adsorbate molecules.

A multilayer adsorption as assumed in the BET theory cannot take place without being disturbed in these narrow pores, for the pore walls put a limitation to the number of adsorbed layers. How much this limitation affects the V_m value calculated from the BET-equation is an important subject of discussion. According to Dubinin [13] the isotherms of type I correspond neither to a multilayer adsorption nor to the progressive completion of a monolayer like in the Langmuir mechanism, but to the filling up of the micropore volume with adsorbate in a liquid like condition. The volume of micropores is thus considered by Dubinin

[30] as the one and only quantity which can be determined from type I adsorption isotherms. Nevertheless after a long debate through the literature, Brunauer and Dubinin [14] came to an agreement on the ranges of applicability of their models: if nitrogen is used as the adsorbate, the BET-model may be applied to microporous solid down to a micropore width of 1 nm whereas the Dubinin model has to be used if "supermicropores" are present i.e. if the pore width is less than 1 nm.

In some cases, in particular for microporous materials, it could be difficult to define the relative pressure range over which the BET plot is linear. Recently a procedure was suggested which allows to determine this *linear BET range* for microporous materials in an unambiguous way [15]. This approach has been recommended in recent standards of the International Standard Organisation (ISO) [16,17].

However, in the every day practice, the BET specific surface area is commonly used whatever the type of microporous solids under investigation but its conventional character must be kept in mind and the corresponding S_{BET} values only considered in comparative experiments.

6.3.3 The Dubinin-Radushkevich (DR) theory

The micropore volume is the only significant quantity which can be derived from type I adsorption isotherm, Dubinin [18] has proposed together with Radushkevich a theory for the calculation of the micropore volume from the low pressure part of the isotherm. This approach leads to the following expression of the isotherm

$$\text{Log } v_a = \text{log } v_o - D (\text{log } p/p_s)^2 \quad (6)$$

where

- v_a is the adsorbed volume of adsorbate per unit mass of adsorbent (m^3 STP/kg)
- v_o is the largest volume of adsorbate which can be condensed in the micropores of an unit mass of adsorbent (m^3 STP/kg)
- p/p_s is the relative pressure
- D is a factor varying with the temperature and the adsorbate/adsorbent pair.

A plot of $\text{log } v_a$ against $(\text{log } p/p_s)^2$ should therefore, be a straight line, the intercept of which, equal to $\text{log } v_o$ would lead immediately to the micropore volume V_o by the following formula

$$V_o = v_o \cdot (\rho_g/\rho_l) \quad (7)$$

ρ_g and ρ_l being the density of the adsorbate in the gas and liquid phase respectively. In the case of nitrogen at 77 K the ratio ρ_g/ρ_l is equal to 0.0015.

For a large number of adsorption systems the DR plot yields indeed a perfect straight line. Frequently, however, the plot is found to deviate from linearity, especially in the high pressure part of the isotherm. In this case, the micropore volume is obtained by extrapolation of the linear part of the DR plot corresponding to the low pressure region of the isotherm.

Nevertheless the micropore volume determination by the DR plot must be limited to nearly pure microporous solids (type I isotherm). If larger pores are also present in the adsorbent (isotherms of type II or IV) the DR method is no longer applicable, for it is not possible to

estimate the relative contributions to the adsorbed volume made by micropore filling and surface coverage. The DR plot has thus a very restricted area of application but provides nevertheless interesting information.

In the frame of the identification of nanomaterials, it could be very interesting to know the micropore volume in order to indicate the possible presence of an internal porosity in the nanoparticles.

6.3.4 Standard isotherms as a tool in textural studies

6.3.4.1 Concept of Standard Isotherm

For a large number of non porous solids, the nitrogen adsorption isotherms did not give any indication of capillary condensation, Several authors like Shull [19], Cranston [20], Lippens and de Boer [21], showed that the ratio between the adsorbed volume, v_a and the volume of the monomolecular layer, v_m , if plotted versus the relative pressure p/p_s could be represented by a single curve called "standard isotherm".

6.3.4.2 The t-method (Lippens and de Boer [21, 22])

By using the concept of "standard isotherm, Lippens and de Boer [21, 22] showed that, if the multi-molecular layer of adsorbed nitrogen could be formed freely on the whole surface, the statistical thickness, t (in nm), of the adsorbed layer could be calculated according to the equation

$$t = 0.354 (v_a/v_m) = f_1 (p/p_s) \quad (8)$$

where v_a and v_m are respectively the volume of nitrogen adsorbed at a relative pressure p/p_s and the volume of nitrogen required to cover the whole surface of the solid substance uni-molecularly, calculated by the BET-equation (1). According to de Boer et al. [22], the thickness, t , of the adsorbed layer of nitrogen, as given by this equation, is nearly independent of the nature of the adsorbent if the latter is non-porous. Consequently, in the absence of capillary condensation, the variation of the statistical thickness of the adsorbed layer of nitrogen with the relative pressure can be filled by a single curve, so called "**the universal t-curve**".

The basic principle of the t-method is to compare the nitrogen adsorption isotherm obtained for a given porous solid with a particular reduced form of a standard isotherm (the t-curve) corresponding to a non porous solid of the same type. To make this comparison, the nitrogen volume, v_a adsorbed at a relative pressure p/p_s on a given sample is plotted as a function of the thickness, t , of the adsorbed layer, as given by the "universal t-curve" for the same relative pressure. Through this v_a - t -plot, valuable information can be obtained about the porous structure of the adsorbent.

As long as the multilayer of adsorbate is formed unhindered on the solid surface, the v_a - t -plot is a straight line passing through the origin, the slope of which is a measure of the surface area of the adsorbent, according to the equation (for nitrogen at 77 K)

$$St = 1.547 \times 10^6 \, dv/dt \quad (9)$$

where t is expressed in nm, v_a in m^3 STP/kg and St in m^2/kg . The subscript t indicates that the specific surface area has been obtained by the t -method.

At higher relative pressures (higher t values), deviations from the straight line may occur

- *an upward deviation* indicates the presence of a capillary condensation in the pores of the adsorbent: this is characteristic of cylinder-shaped pores, "ink-bottle" pores or spheroidal cavities
- *a downward deviation* is observed when micropores or slit-shaped pores are present in the solid.

The v_a - t -plot is an interesting tool in textural studies for it gives a measure of the specific surface area of the adsorbent as well as valuable information on the shape of pores. Moreover it is worthwhile to point out that the manner in which the v_a - t -plot deviates from the straight line is also characteristic of the pore-size distribution in the solid. For example, the higher the pressure at which deviation occurs, the larger the size of the pores.

Other interesting characteristics of the t -plot are on the one side, the possibility of obtaining micropore size distribution and on the other side **the possibility of distinguishing internal and external surface area of particles.**

6.3.4.3 Limitations of the t -method

There are some discrepancies appear among the published versions of the "standard isotherms", two different approaches have been taken from the literature. On the one hand Sing [23-25] and his co-workers put forward the necessity for building up a series of standard isotherms, each of them corresponding to several samples of the same chemical nature, for example, a standard isotherm for silica, another one for alumina and so on.

On the other hand, Lecloux [26-28] and his group proposed a new set of standard isotherms including the reference data of Sing and demonstrated that each of them corresponds to a definite strength of interactions between adsorbent and adsorbate. The fact of classifying the standard isotherms according to the intensity of adsorbate-adsorbent interactions has been proved to be a very interesting and general one [28]. The same set of standard isotherms may indeed be successfully applied whatever the nature of the adsorbent-adsorbate pair.

6.3.4.4 The α_s method (Sing [23, 24])

The same principle of comparing an experimental isotherm to a standard one is applied in a slightly different way by Sing [23]. This author modifies the t -method by replacing the thickness, t , of the adsorbed layer by the ratio (v_a/v_x) , so called α_s where v_x is the amount adsorbed by a non porous reference solid at the selected relative pressure $(p/p_s)_x$. By doing this, he defines a new type of reduced standard isotherm by plotting α_s versus p/p_s according to the equation

$$\alpha_s = (v_a/v_x) = f_2(p/p_s) \quad (10)$$

In principle α_s could be set equal to one at any convenient point on the standard isotherm. According to Sing [24] it is usually convenient in practice to set $\alpha_s = 1$ for $(p/p_s) = 0.4$ since monolayer coverage and micropore filling generally occur at $p/p_s < 0.4$ whereas capillary

condensation takes place at higher p/p_s values.

If the $v_a - \alpha_s$ -plot is constructed as the amount adsorbed on the test sample versus the α_s - values for the standard isotherm, another means of comparing the mathematical form of isotherms is obtained. The shapes of the $v_a - \alpha_s$ -plots are essentially the same as those of the v_a -t-plots and the deviations from linearity are explained in the same way.

There are however two main differences between the t- and the α_s -method:

- The first one, as already mentioned, lies in the choice of the standard isotherm. According to de Boer, the "t-curve" is nearly independent of the nature of the adsorbent and consequently the standard isotherm is obtained by averaging several reduced isotherms corresponding to various non porous solids. On the contrary, Sing chooses the standard isotherm adapted to the nature of the test sample. He indeed determined standard α_s -curves for nonporous hydroxylated silica and for non porous alumina.
- The second difference between α_s - and t-methods, as claimed by Sing [25], lies in the fact that the α_s -method would be independent of the BET-method, while the t-method obviously fall into the field of the BET-method by using, in the definition of t, the value, v_m of the BET monolayer capacity. See equation (8). This question has been much debated in the literature, but Lecloux [28] showed that the t- and α_s - methods are strictly relevant to the BET-theory and that these two methods are two equivalent ways of analyzing adsorption isotherms.

6.3.4.5 The n-method (Lecloux [26-28])

The basic principle of the t- and α_s -methods, i.e. the comparison between test and standard isotherms, was somewhat extended by Lecloux who introduces a general criterion in the selection of standard isotherms. He pointed out that the thickness of the adsorbed layer on a non-porous solid not only depends on the relative pressure, but also on the magnitude of the adsorbent- adsorbate interactions [28]. Consequently, the standard isotherm must be chosen according to these interactions and not merely on the basis of the chemical nature of the test sample.

As one of the easiest way of expressing the intensity of adsorbate-adsorbent interactions is to use the C_{BET} constant value (see for example equation 2) a new set of five standard isotherms was proposed, each of them corresponding to a definite range of the C_{BET} value between 20 and 3000. These reference isotherms are used in the following reduced form:

$$n(C_{BET}) = v_a/v_m = f(p/p_s, C_{BET}) \quad (11)$$

where v_m is calculated by the BET equation. These standard data are illustrated in Figure 22 and the corresponding numerical values are given in

Table 12.

The comparison between test and standard isotherms is made by constructing the $v_a-n(C_{BET})$ -plot where v_a is the amount adsorbed on the test sample and $n(C_{BET})$ is the standard value chosen according to the C_{BET} constant characteristic of the test isotherm. The shapes of the $v_a-n(C_{BET})$ -plots are essentially the same as those obtained with the v_a-t - or the $v_a - \alpha_s$ -plots and the deviations from linearity are explained in the same way.

But the main advantage of the n-method is the fact that the simple reduced form defined by the equation (11) is the only suitable form to compare isotherms obtained with different adsorbents. Moreover, the whole set of standard isotherms obtained from nitrogen adsorption has been demonstrated to be suitable for other adsorbates [28]. *The reference data, presented in Figure 22 and Table 1, can thus be used whatever the nature of the adsorbent and of the adsorbate.* (Copy of the data published in [28, 29])

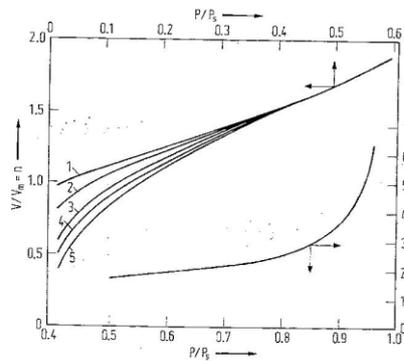


Figure 22 Reference isotherms in the n-reduced form. Each curve corresponds to a definite range of C_{BET} values: n1 for $C_{BET} \geq 300$; n2 for $300 \geq C_{BET} \geq 100$; n3 for $100 \geq C_{BET} \geq 40$; n4 for $40 \geq C_{BET} \geq 30$ and n5 for $30 \geq C_{BET} \geq 20$

Table 12 Numerical values of the reference isotherms in the n reduced form

Table 1. Numerical values of the reference isotherms in the n reduced form

Range of validity	$c_{BET} \geq 300$	$300 \geq c_{BET} \geq 100$	$100 \geq c_{BET} \geq 40$	$40 \geq c_{BET} \geq 30$	$30 \geq c_{BET} \geq 20$	Range of validity
p/p_s	n_1	n_2	n_3	n_4	n_5	p/p_s
0.02	0.972	0.805	0.593	0.503	0.401	0.02
0.03	0.992	0.853	0.669	0.575	0.489	0.03
0.04	1.017	0.893	0.718	0.635	0.545	0.04
0.05	1.034	0.920	0.763	0.686	0.602	0.05
0.06	1.048	0.946	0.802	0.730	0.647	0.06
0.07	1.062	0.966	0.839	0.768	0.692	0.07
0.08	1.076	0.992	0.870	0.804	0.729	0.08
0.09	1.090	1.011	0.901	0.838	0.768	0.09
0.10	1.102	1.037	0.929	0.868	0.808	0.10
0.12	1.127	1.068	0.983	0.924	0.872	0.12
0.14	1.155	1.105	1.028	0.976	0.932	0.14
0.16	1.184	1.136	1.071	1.022	0.983	0.16
0.18	1.209	1.167	1.113	1.066	1.034	0.18
0.20	1.234	1.203	1.153	1.110	1.082	0.20
0.22	1.260	1.234	1.192	1.154	1.127	0.22
0.24	1.285	1.263	1.232	1.195	1.175	0.24
0.26	1.311	1.297	1.266	1.235	1.218	0.26
0.28	1.339	1.325	1.305	1.275	1.257	0.28
0.30	1.367	1.356	1.339	1.320	1.299	0.30
0.32	1.395	1.384	1.373	1.370	1.342	0.32
0.34	1.427	1.415	1.407	1.407	1.384	0.34
0.36	1.452	1.452	1.444	1.444	1.424	0.36
0.40	1.511	1.511	1.508	1.508	1.497	0.40
0.42			1.536			0.42
0.44			1.565			0.44
0.46			1.596			0.46
0.48			1.630			0.48
0.50			1.667			0.50
0.55			1.757			0.55
0.60			1.864			0.60
0.65			1.983			0.65
0.70			2.127			0.70
0.75			2.280			0.75
0.80			2.528			0.80
0.85			2.853			0.85
0.90			3.588			0.90
0.95			5.621			0.95

In the n-method, the set of standard isotherms has been determined once for all and covers a very large range of adsorbent-adsorbate interactions. In fact, the use of the n-method suggests the existence of a continuous variation of the standard isotherms as a function of the C_{BET} values. This continuum has been proved [28] to be fitted with a good accuracy (within 5 %) up to a relative pressure of 0.65, by the following equation

$$n(c_{BET}) = \frac{v_a}{v_m} = \frac{kx}{1 - kx} \cdot \frac{[1 - (m + 1)(kx)^m + m(kx)^{m+1}]}{\left[\frac{1}{c_{BET}} + \frac{c_{BET} - 1}{c_{BET}} kx - (kx)^{m+1} \right]} \quad (12)$$

where x is the relative pressure p/p_s . The values of k and m were calculated so as to be the same for all the curves and equal to 0.95 and 4.18 respectively. In these conditions, the only characteristic parameter is the C_{BET} constant.

The n-method puts forward that the only parameter for choosing the right standard isotherm is the adsorbate-adsorbent interaction intensity, expressed by the C_{BET} constant value. If this choice is correctly made, the straight line corresponding to the low relative pressures in a $v_a-n(C_{BET})$ -plot always pass through the origin. But if the right reference data are not used, this straight line cuts the v_a -axis for a positive or a negative value of the adsorbed volume according to whether the C_{BET} constant of the test isotherm has a higher or a lower value than the C_{BET} value of the standard isotherm used.

This phenomenon is illustrated of Figure 23 as well as the proportionality between the three methods

$$t = 0.354 n(C_{BET})$$

$$t = 0.358 \alpha_s$$

$$\alpha_s = 0.658 n(C_{BET})$$

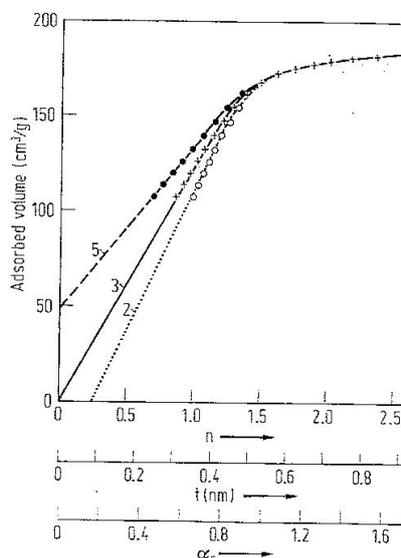


Figure 23 Comparison of $v_a - t$, $v_a - \alpha_s$ and $v_a - n$ plots obtained on a silica alumina sample with a BET surface area of $539 \text{ m}^2/\text{g}$ and a C_{BET} value of 68. The numbers refer to the standard isotherms used as in Figure 22. Only the right choice of the standard isotherm gives a straight line passing through the origin, as it should be.

6.3.4.6 Applications and limitations of the use of Standard Isotherms

The n-Method and the Assessment of Porosity

- Specific surface area measurement

If the right reference isotherm is used to analyze an unknown sample, the $v_a-n(C_{BET})$ plot is, in the low pressure region, a straight line passing through the origin. The slope of this line is a measure of the specific surface area according to the equations:

$$S_n = 0.465 \times 10^6 \frac{dv_a}{dn(C_{BET})} \quad (13)$$

the numerical value of the proportionality factor being given for nitrogen at 77 K and the n-subscript indicating that the n-method has been used to calculate the specific surface area.

The only condition to obtain an excellent agreement between the S_n and the SBET

value of the surface is the **correct choice of the standard isotherm**. If the right reference data are not used, the only way to determine the specific surface area is from the slope of the tangent to the curve $v_a - n(C_{BET})$ through the origin, The surface area value obtained in this way is lower or higher than the BET -value if the chosen reference isotherm is characterized by a C_{BET} -value respectively higher or lower than the C_{BET} value of the isotherm under test. This incorrect way of calculating the surface is too often practised in the literature when the t - or the α_s -method is used with incorrect standard data.

- Assessment of microporosity - Method of Brunauer [30,31]

It has already been noted that the way in which a v_a - t , a v_a - α_s or a v_a - n plot deviates from linearity is indicative of the pore size distribution of the sample. But experimentally, it appears (see Figure 23 for example) that the shape of these plots can be strongly affected by the choice of the standard isotherm. Consequently, if such a plot is used to characterize the porosity of a sample, it is essential to choose the right standard isotherm according to the C_{BET} constant value before performing any analysis of the curve-shape. A similar remark has been made by Brunauer et al. [30] in their paper describing a method of analyzing the microporosity of a sample on the basis of the v_a - t -plot shape.

The basic principle of *Brunauer's method* is to consider that equation (9) can be applied to every point of the v_a - t curve, if this curve shows a downward deviation from linearity. In other words, if micropores or slit-shaped pores are present in the solid, at any point of the isotherm, the surface area accessible to further adsorption decreases as the thickness of the adsorbed layer increases and the slope of the tangent to the v_a - t curve at a given t - value is proportional to the accessible surface area after a layer of thickness t has been adsorbed on the solid. As no capillary condensation occurs in slit-shaped pores or in micropores, the filling of a pore takes place by the

coalescence of the adsorbed layers on its opposite walls. At this moment, the thickness of the adsorbed layer is equal to half a pore width: $d = 2t$.

To evaluate the pore size distribution [31-32] on this basis, the v_a - t plot is divided into k steps, each corresponding to an increase Δt in the thickness of the adsorbed layer. At the beginning and the end of each step a tangent to the v_a - t -curve is drawn and the respective slopes are converted into surface area S_k and S_{k-1} by use of equation (9). The difference $\Delta S_k = S_k - S_{k-1}$ is equal to the surface of those pores having a width lying between $(2 t_k - \Delta t)$ and $(2 t_k + \Delta t)$. The curve $\Delta S_k / 2 t_k$ against $d_k = 2 t_k$ directly express the distribution of pore surface as a function of pore width. To calculate the

pore volume distribution it is necessary to define a relationship between the volume, v , and the surface, s , of a pore i.e. to choose a pore model. In the case of slit-shaped pores of width d , the ratio v/s is equal to $d/2$, whereas for cylindrical pores of radius r , the ratio v/s is equal to $r/2$.

The Brunauer's analysis of the v_a - t plot is at the present time **the only mean of calculating the pore size distribution of micro pores from one isotherm**. Even if the theoretical bases of the method are within the limits of the BET theory [32], it is the only practical way of comparing various microporous solids providing that the reference isotherm used to construct the v_a - t plot is chosen, in each case, on the basis of the C_{BET} value [28].

It is worth noting that Brunauer's analysis may be extended to the v_a - n plots and thus performed whatever the adsorbent-adsorbate pair. The distribution of pore surface as a function of pore width can be calculated if the statistical thickness of a monolayer of adsorbate is known. In the case of nitrogen adsorption at 77°K, the analysis will be based on equation (13).

The n-method to assess the external surface area of primary particles and their aggregation stage

The basis of this method is **the use of the t-plot** as proposed by de Boer and modified by Lecloux (Lecloux 1979) to take into account the level of adsorbant-adsorbate interaction expressed by the C_{BET} value.

Several interesting pieces of information can be derived from the t-plot, in particular the total surface area S_t which is comparable to BET surface area S_{BET} and the external surface area of the particle S_w . Moreover the shape of these plots combined with the shapes of the nitrogen adsorption isotherms are also very informative. Several examples are given in Figure 24 to Figure 29.

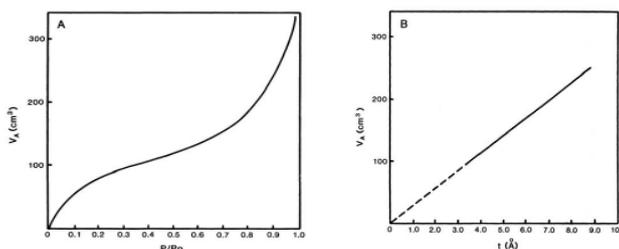


Figure 24 Isotherm of type II and linear t-plot. It corresponds to agglomerates of non porous nano or non-nano particles depending of the surface area value or the VSSA value.

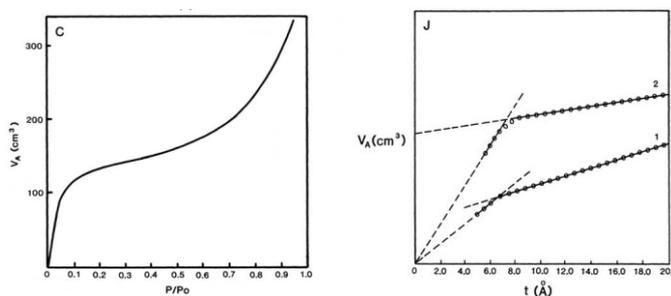


Figure 25 Isotherm of type IV and two straight lines t-plot. It corresponds either to aggregates of porous non-nano-particles or to small aggregates of non-porous nano-particles.

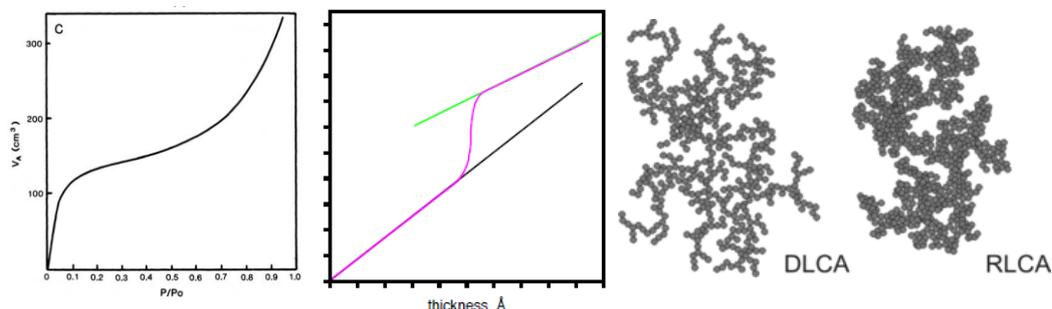


Figure 26 Isotherm of type IV and two straight lines t-plot. It corresponds to agglomerates of non-nano-particles or large aggregates of non-porous nano-particles as illustrated.

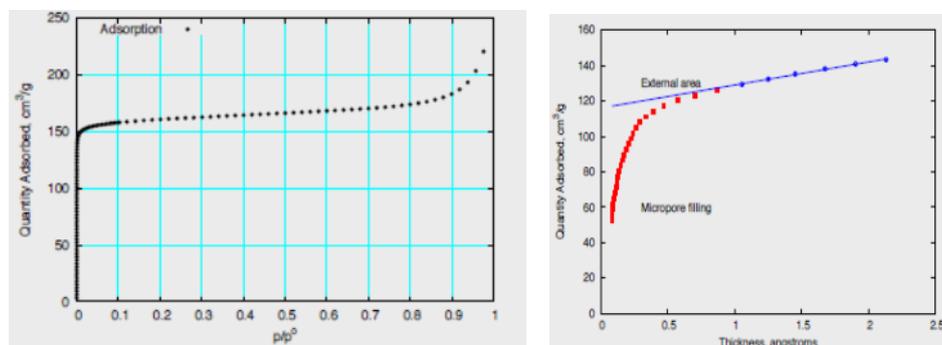


Figure 27 Isotherm of type I and two straight lines t-plot. It corresponds to strongly aggregated nano-particles or to nanostructured nanomaterials.

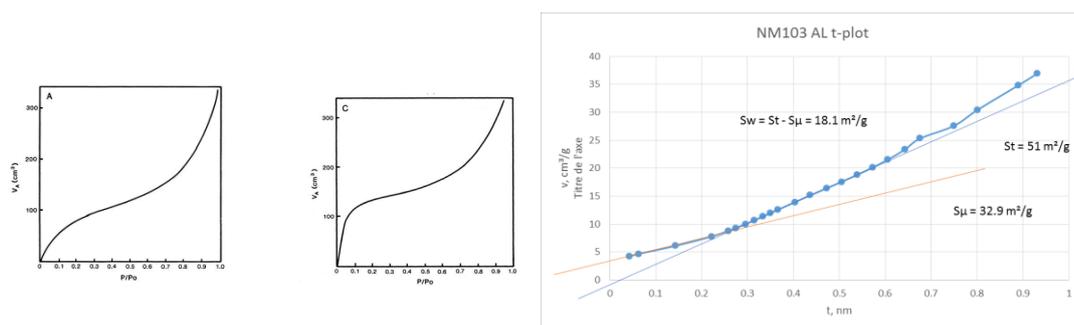


Figure 28 Isotherm of type II or IV and two straight lines t-plot. It corresponds to microporous non aggregated nanoparticles like CNT or coated TiO2.

An in depth analysis of the isotherms and of the corresponding t-plots can then provide interesting insight in the texture and the nano character or not of the sample. Of course, in a few cases, some ambiguities could remain that can be solved by a qualitative electron microscopy picture.

Limitations of the use of standard isotherms

The use of standard isotherms to characterize the porosity of solids through the t -, the α_s - or the n -method is submitted to the same limitations as the BET model, for all these methods have been demonstrated to be directly or indirectly relevant to the BET-theory [28, 32]. But, in spite of its theoretical simplicity the BET-model has been experimentally proven [28, 32, 33] to have a very wide range of applicability. In the same way, the practical usefulness of the standard isotherms and the methods based upon largely exceeds their theoretical validity, for at the present time there is no other method which can give, in such a simple way, the same qualitative and quantitative information on the porous texture of solids. It is necessary however to keep in mind that the porous solids have been "seen" through a rather simple model and that the reality may be more complex than the pictures obtained in this way.

6.3.5 Porous Texture of Solids in the Mesopore-Size Region

6.3.5.1 Introductory Remarks

A porous texture can be considered as a collection of elements in pore space, each characterized by shape, size and relative allocation with respect to other elements in pore space. In practice however, the information on pore texture will seldom be as detailed as that. Only information concerning size, surface and volume in pore space will generally be available. The shape of the pores for actual porous texture is often so difficult to define that, in common practice a predominant pore shape is assumed rather than established independently. But this assumed pore shape has a critical influence on the pore size distribution calculated from nitrogen adsorption data.

Pore-size analysis is traditionally based upon the application of Kelvin's relation between vapour pressure of a capillary condensed phase and pore size. But Kelvin's relation was developed for large size capillaries and basically ignores physical adsorption of the adsorbate on the pore walls. This phenomenon is of importance for pores in the meso-size range and necessitates therefore additional correction terms to Kelvin's relation. This fact was already pointed out by Deryagin [34] in 1940 on the basis of thermodynamic reasoning and emphasized by Broekhoff and de Boer [35-37] who developed a complete thermodynamical analysis of physical adsorption and capillary condensation phenomenon. Unfortunately, this approach has too largely been ignored by subsequent authors in the field.

6.3.5.2 Thermodynamics of Vapour Sorption in Capillaries

By including physical adsorption into the thermodynamic treatment of capillary condensation and evaporation and putting forward the Gibbs Maximum Work Principle, Broekhoff developed the formal framework for estimating pore size distributions of mesoporous solids. It appears that Kelvin equation cannot be used as such but should be corrected to account for the multilayer adsorption which takes place even on non porous solids and is represented by the standard isotherms. This multilayer adsorption depends on the adsorbate-adsorbent interactions (as expressed by the CBET constant) but also

on the curvature radius of the surface i.e. on the shape and the size of the pores in which the adsorption takes place.

Although Broekhoff and de Boer published separate papers on adsorption in- and desorption from capillaries of various shapes, it is possible to summarize their results [38] by introducing a *shape factor*, f , which has to be taken equal to 1 for slit shaped pores, to 2 for tubular type pores and to 3 for "ink-bottle" type pores or spheroidal cavities. In these conditions de Broekhoff-de Boer model (*BdB model*) leads to the following results:

- *the thickness t of the adsorbed layer in a pore of radius r_p is given at a relative pressure p/p_s , by:*

$$-\ln(p/p_s) = F(t, c_{\text{BET}}) = \frac{(f-1) \sigma_{\text{lv}} V_m}{RT (r_p - t)} \quad (14)$$

where σ_{lv} and V_m are respectively the surface tension and the molar volume of the liquid adsorbate at the absolute temperature T . It is worth noting that, if r_p tends to infinity (non porous solids) the equation (14) tends to the analytical expression of the standard isotherm $F(t, c_{\text{BET}})$. This is obtained by introducing $n(c_{\text{BET}}) = t/0.354$ in equation (12)

- *during the adsorption the capillary condensation in a pore of radius r_p occurs for a critical thickness t_{cr} of the adsorbed layer, the value of which is solution of:*

$$\frac{dF(t, c_{\text{BET}})}{dt} = \frac{(f-1) \sigma_{\text{lv}} V_m}{RT (r_p - t)^2} \quad (15)$$

the relative pressure p/p_s at which the capillary condensation occurs in a pore of radius r_p is obtained by introducing in the equation (14) the value of t_{cr} given by equation (15).

- *during the desorption, the evaporation of the condensed vapour from a pore of radius r_p occurs at a relative pressure p/p_s solution of*

$$r_p - t_e = \frac{f \sigma_{\text{lv}} V_m}{RT \ln(p_s/p)} + \frac{\int_{t_e}^{r_p} f \cdot (r_p - t)^{f-1} F(t, c_{\text{BET}}) dt}{(r_p - t_e)^{(f-1)} \ln(p/p_s)} \quad (16)$$

where t_e is the value of t given by the relation (14). Equation (16) is called by Broekhoff and de Boer "*the modified Kelvin equation*".

6.3.5.3 Distribution of pore area and pore volume

To calculate the distribution of pore area and pore volume as a function of pore size, the isotherm is divided into a suitable number of intervals, each of them corresponding to a

small relative pressure range defined by its mean value. The calculation is worked downwards from saturation and for the k^{th} interval, characterized by a pressure p_k , the specific surface area, S_k and the volume V_k of the pores of radius r_{pk} are given by:

$$\begin{cases} S_k = \frac{f r_{pk}^{(f-1)}}{(r_{pk} - t_{k,k})^f} \left[Q \cdot \Delta V_k - \sum_{i=1}^{k-1} \frac{S_i}{f \cdot r_{pi}^{(f-1)}} \left[(r_{pi} - t_{i,k})^f - (r_{pi} - t_{i,k-1})^f \right] \right] \\ V_k = S_k \cdot r_{pk} / f \end{cases} \quad (17)-(18)$$

where

ΔV_k is the variation of the adsorbed or desorbed volume on the k^{th} interval (in m^3 STP gas/kg of adsorbent)

Q is the ratio of the molar volumes of the adsorptive in the liquid and in the gas phase

f is the shape factor as defined in paragraph 8.2.

r_{pk} and $t_{k,k}$ are the solutions of equations (14) and (15) if the adsorption branch of the isotherm is considered, and of equations (14) and (16) if the desorption branch is used $t_{i,k}$ for $i = 1, \dots, (k - 1)$, are the solutions of equation (14) for each pair p_k, r_{pi}

The relations (17) and (18) have been obtained according to a line of reasoning similar to the one developed by Barrett, Joyner and Halenda [39] in their simple BJH method based on a cylindrical pore model and the uncorrected Kelvin-equation. The relations proposed by these authors are only a particular limiting case of equations (17) and (18). The latter are of general interest, for they are applicable to both adsorption and desorption isotherms, whatever the pore shape and the adsorbent-adsorbate interactions.

By plotting as a function of r_k the values of S_k and V_k calculated by equations (17) and (18), the distributions of pore area and pore volume with respect to pore size are obtained. The *cumulative* specific surface area S_{cum} and the cumulative pore volume V_{cum} are defined by the sum on k of all the S_k or V_k values.

6.3.5.4 Validity of the BdB model

First of all, the method developed by Broekhoff-de Boer [35] and generalized by Lecloux [38] is strictly limited to pore size distributions in the **mesopore range** (i.e. 2 and 30 nm). For narrower pores, the capillary condensation phenomenon does not exist and the BdB model is purposeless. For wider pores, the capillary condensation phenomenon occurs at pressures very near the saturation i.e. at relative pressures close to unity. For these p/p_s values, the equations (14) to (16) of the BdB model have such a mathematical structure that the pore radius value is very sensitive to a small variation of the pressure. Consequently, a slight inaccuracy in the experimental determination of the pressure near the saturation point leads to an unacceptable lack of precision in the definition of the pore size.

The main limitation of the applicability of the BdB method comes from the irreversible

nature of vapour sorption in mesopores and thus the application of equilibrium thermodynamics could lead to over- or underestimates pore sizes. But this uncertainty can be removed by choosing specific simple pore models. Equations (14) to (16) have been developed for three types of pores [35, 38] :

- *for slit shaped pores* ($f = 1$), only the desorption branch can be used to calculate pore size distribution from equations 14 and 16
- *for cylindrical pores* ($f = 2$). pore size distribution can be calculated both from adsorption branch (with equations 14 and 15) and desorption branch (with equations 14 and 16) of the hysteresis loop. Ideally, i.e., if the actual porous system is very well described by the cylindrical pore model. Both distribution curves should coincide and in both cases the total cumulative pore surface area S_{cum} should be nearly equal to S_{BET} (unless micropores are present, in which case S_{cum} remains smaller than S_{BET}). In practice, some discrepancies may occur because of the inadequacy of the cylindrical pore model for the solid considered. For example, the fact that S_{cum} appears substantially larger than S_{BET} for the desorption branch but not for the adsorption branch is indicative of bottle-neck effects in the pore and of irreversibility of the desorption branch.
- *for "ink-bottle" pores or spheroidal cavities* ($f = 3$), only the adsorption branch can be used to calculate pore size distribution from equations 14 and 15. According to Broekhoff [37], the same applies to pores of irregular shape. In this case one can seldom expect evaporation to be a reversible process.

An other aspect of the irreversibility of vapour sorption arises from the fact that in actual porous systems, pores of different sizes are mutually interconnected, so that emptying of an element of the pores network can only occur if there is at least one connecting, emptied pathway to the external environment. There is however reason to believe that for pore filling during adsorption, network effects are much less important and a relation of the type of equation (15) leads to a quite satisfactory estimate of the pore size.

Even if it is important to proceed with caution in any attempt to calculate pore size distribution from vapour sorption data, the systematic use of BdB method with a good working model for the pore shape and the right choice of the standard isotherm generally leads to a qualified and self-consistent picture of the porous texture of the analyzed sample. In fact, the generalized "BdB method" is, at the present time, the only method which can be successfully applied to both adsorption and desorption branches of the isotherm for various pore shapes and whatever the adsorbate-adsorbent interaction.

One of the main interests of this method is that *the cumulative specific surface area, S_{cum} is much more consistent with the S_{BET} value than the S_{cum} value obtained by any other method.* Moreover, by using synthetic samples of well defined porous structure, Scholten [40, 41] demonstrated that the BdB model gives pore size distributions much closer to the reality than those given by other models. Finally, by introducing in the BdB model various reference t-curves, directly derived from the $n(C_{BET})$ standard data given in

Table 12, it is possible to calculate pore size distribution whatever the adsorbate-adsorbent pair. In these conditions the pore size distribution of a given solid can be calculated from sorption isotherms of different vapours and the results compared to each other. It appears that a very good agreement can be obtained if, in the BdB model, the reference isotherm $F(t, C_{\text{BET}})$ is chosen according to the adsorbate-adsorbent interactions [42].

6.3.5.5 Mesoporosity and nanomaterials

In the case of nanomaterials, the porous texture in the mesopore-size region can provide interesting information on the state of agglomeration and/or aggregation of the primary particles.

As already said, isotherm of type I are representative of strongly aggregated nano-particles or of nanostructured nanomaterials. Isotherms of type II or IV indicate the presence of apparent porosity that can be due to internal porosity of the particles or aggregates or to the voids between these aggregates if they are more or less agglomerated or aggregated.

The larger the aggregates, the larger the voids between them will be. Moreover the size of the internal porosity of aggregates will reflect their degree of aggregation, a loose aggregation leading to large mesopores while a strong aggregation to smaller pores down to micropores. If the particles are only agglomerated, there will be no hysteresis loop and the t -plot will be a straight line passing through the origin.

6.3.6 Practical Analysis of Adsorption Isotherms

The various theories and models presented in the previous sections are applicable with the nature of the vapour, which is physically adsorbed on the surface of a given solid. The practical applications of these theories however are almost limited to the analysis of adsorption-desorption isotherm of nitrogen at 77 K. This adsorptive is widely used because of its chemical inertness at low temperature, its availability at a high purity level and also because the small size of the nitrogen molecule allows itself to penetrate in very narrow pores.

To turn the analysis of sorption isotherms to the best account it is necessary to systematically apply the various models and methods described in the previous sections. In the laboratory practice, it is very useful to always apply the same systematic procedure to analyze the sorption isotherms. It is the only way to obtain the most realistic picture of the porous texture of the solid under test. It is very convenient to proceed as follows.

- General inspection of the isotherm: from the shape of isotherm and its hysteresis loop, the adsorbent can be inferred as a microporous, mesoporous or macroporous solid (see Figure 19 and Figure 20).
- Application of the BET model to calculate both the BET specific surface area S_{BET} and the C_{BET} constant which is a measure of the intensity of adsorbate-adsorbent interaction. As already pointed out, the knowledge of the C_{BET} value is essential for the right use of the n -method as well as for the application of the generalized BdB model.
- Application of the n -method: If the right standard isotherm is used to take into account the adsorbate-adsorbent interaction, the v_a - n -plot appears in the various

shape presented in chapter 7.6.2. In most cases, the low pressure region is a straight line passing through the origin. From the slope of this line, the value S_n of the specific surface area can be calculated. At higher pressure, the shape of the v_a - n -plot is indicative of the type of pores present in the solid :

- a straight line passing through the origin corresponds to a pure macroporous or non-porous solid and its slope depend on the size of the particles;
- an upward deviation can be associated with cylindrical or spheroidal mesopores; these pores are generally formed by aggregation of
- a downward deviation indicates the presence of micropores or slit shaped pores.
- In some cases, a second straight line is found at higher relative pressures. This may be considered as representing the adsorption in wide pores or on the external surface of porous particles, the surface area of which, S_w can be calculated from the slope of this second straight line:

$$S_w = 0.465 \times 10^6 \frac{dv_a}{dn}$$

Moreover as stated before, the downward deviation of the v_a - n -plot can be used to evaluate the micropore size distribution by the Brunauer method or at least, the micropore volume by the Dubinin plot.

- Assessment of the mesopore volume: An accurate estimate of the mesopore volume V_{mp} is essential to yield a correct calculation of the pore size distribution. If the sorption isotherm shows a clearly defined plateau in the vicinity of $p/p_s = 1$, then complete mesopore filling may be assumed and the total mesopore volume V_{mp} is determined by the adsorbate uptake at the plateau. In a number of cases, however, the adsorption isotherm shows asymptotical behaviour around $p/p_s = 1$. In this case the upper closing point of the hysteresis loop may be used for assessing the mesopore volume V_{mp} but interference with the presence of macropores cannot be excluded. If no clearly developed hysteresis loop is found, then the macropore system is predominant and no mesopore volume can be calculated. A common practice, however, tends, in this case, to define V_{mp} as the volume of adsorbate taken up at a relative pressure very close to the saturation, c.g. at $p/p_s = 0.98$. This practice is potentially dangerous and should be exercised with care for it could lead to false conclusions on the mesopore distribution.
- Pore size distribution calculation
The BdB method based on equations (14) to (18) will systematically be applied to adsorption and desorption branches of isotherms, for different shapes of capillaries, the standard isotherm being chosen according to the C_{BET} value characteristic of the isotherm under test. Consequently, different curves giving the distribution of pore volume and pore area with respect to pore size are obtained. To choose the curve which will lead to the most realistic picture of the pore structure of the analyzed sample, all the information acquired during the preceding steps of this analysis must be taken into account. The pore shape model must be consistent with the type of hysteresis and the shape of the n -plot, and the cumulative specific surface area, S_{cum} should be nearly equal both to the S_{BET}

and the S_n values.

- Final discussion

The various methods of analyzing sorption isotherm and the results they give must lead to a coherent picture of the porous texture of the sample under test. Finally a balanced judgement should be made between the information coming from the methods, bearing in mind the approximate nature of each of them. It is wise to support this judgement by using independent information coming for instance from structural studies or electron microscopy.

The different steps in the analysis of sorption isotherms and the way they are interconnected is summarized in Figure 29. Even if a reasonably self-consistent picture of the porous texture of a solid can be obtained in this way, it is important to keep in mind that such a picture is based upon a series of simplifications of reality. Pictures of different solids obtained through the same approach can however be used to make quantified comparison, which is the most interesting point for practical purposes.

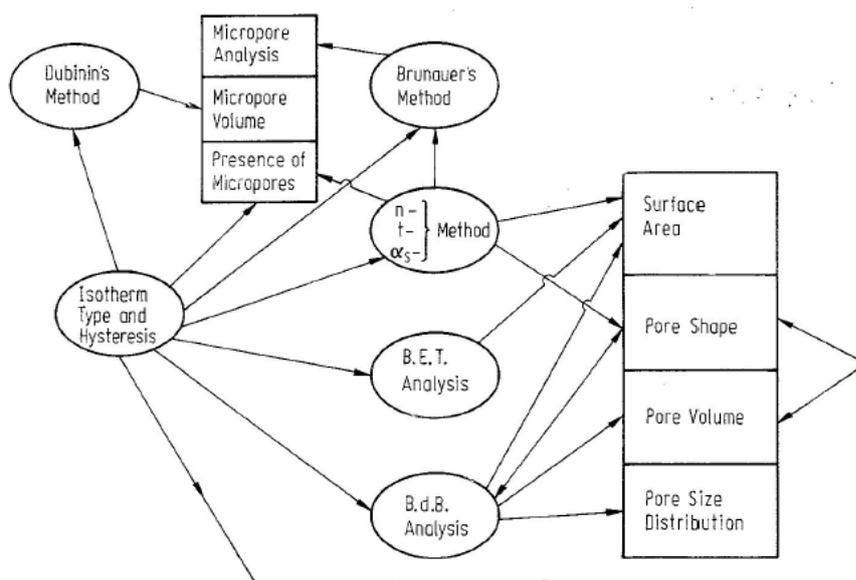


Figure 29 The different steps of the analysis of sorption isotherms and the way they are interconnected.

Remark: The proposed experimental and analysis scheme is in line with the following ISO norms: ISO 15901-1:2005; ISO 15901-2:2006; ISO 15901-3:2007; ISO/TS 17200:2013 and ISO 9277:2010

6.4 References

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