

RELATIONSHIP BETWEEN THE SPECIFIC SURFACE AREA PARAMETERS DETERMINED USING DIFFERENT ANALYTICAL TECHNIQUES

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1. INTRODUCTION

Specific surface area is a major physical property to be taken into account in characterising the raw materials used in the ceramic industry because its value conditions the behaviour (flowability, reactivity, etc.) of these materials in the different manufacturing process stages [1].



Figure 1 Specific surface area of an irregular particle.

The analysis technique, par excellence, for determining the specific surface area of solid or powder materials, is volumetric gas adsorption. This technique evaluates the quantity of gas adsorbed on the surface of the material as a function of the applied partial pressure and, using an appropriate theoretical model in accordance with the type of sample to be analysed, it calculates the sample's specific surface area. Different theoretical models can be applied but, in the case of ceramic materials, specific surface area is calculated using the BET

(Brunauer, Emmett, and Teller) model, based on the adsorption of a monomolecular layer of nitrogen on the surface of the sample, in accordance with Equation 1 [2]. The selection of the type of gas (nitrogen, krypton, argon, etc.) depends on the affinity of the gas for the analysed surface.

$$\frac{1}{v \left[\left(\frac{P}{P_0} \right) - 1 \right]} = \frac{c-1}{v_m} \left(\frac{P}{P_0} \right) + \frac{1}{v_m c} \quad (1)$$

Where: v , adsorbed gas volume; P , applied pressure; P_0 , saturation pressure, v_m , gas volume needed to create a monomolecular layer of nitrogen; and c , the BET equation constant.

Since specific surface area is intimately linked to particle size, this study was undertaken to establish whether the results obtained from the determination of particle size distribution could be correlated with those of specific surface area, as other factors influence the latter parameter, such as the microstructure of the materials. Particle size determination might, thus, be considered an indirect analysis technique for the estimation of specific surface area. Particle size determination by the laser diffraction technique [3] allows, a priori, the specific surface area of materials to be obtained from the particle size distribution data, and other physical parameters such as material density from Equation 2.

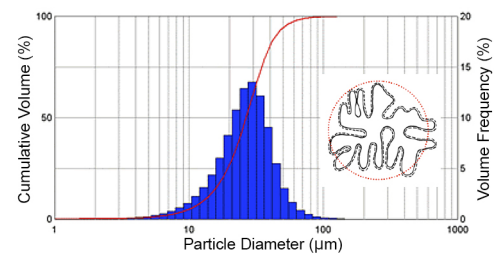


Figure 2. Particle size distribution.

$$S_e = \frac{6 \sum \frac{V_i}{d_i}}{\rho \sum V_i} = \frac{6}{\rho D_s} \quad (2)$$

where: V_i , relative volume by particle size class d_i ; ρ ; material density; and D_s , mean diameter based on surface area, also known as the Sauter diameter.

The use of these analysis techniques allows different key properties to be obtained from a single measurement. Thus, thanks to their versatility, a material can be characterised more effectively in a shorter time. However, it is necessary to study and evaluate whether the results obtained indirectly are satisfactory in each case.

2. OBJETIVE

The main objective of this paper is to compare the results obtained in the calculation of the specific surface area of materials of different ceramic nature using two different analysis techniques (gas adsorption and laser diffraction) and to study the possible correlation between the values obtained by both techniques, determining any limitations of these techniques, and verifying the correlatability of the result.

3. METHODOLOGY AND MATERIALS

3.1. INSTRUMENTS

The techniques selected for establishing the correlations in the determination of the specific surface area were the gas adsorption and wet laser diffraction techniques.



Figure 3. instruments for the determination of the specific surface area of materials
a) Nitrogen adsorption instrument, b) Wet laser diffraction instrument.

In the first case, using nitrogen gas as adsorbent, the adsorption curves were determined with a Micromeritics TriStar 3000 instrument, following the static volumetric method according to standard ISO 9277:1995. The specific surface area was determined according to the BET method from this adsorption isotherm, in accordance with Equation 1.

The second studied technique, wet laser diffraction, allows the particle size distribution of the test sample to be determined as direct parameter. The distribution was determined using a MALVERN MASTERSIZER 2000 laser diffraction instrument. In this instrument, the particles cross a laser light beam and the scattered light is collected at 52 detectors.

The particle size distribution is used to calculate characteristic particle diameters such as d_{50} and the Sauter mean diameter (d_s). D_{50} is the diameter below which 50% by volume of the total particles is found. Parameter d_s is the mean surface diameter, defined as the diameter of a sphere with the same surface area as the particle. As mentioned previously, the value of the specific surface area is determined indirectly by this technique from the Sauter mean diameter, using Equation 2.

3.2. MATERIALS

In a first study stage, different reference materials with a certified specific surface area were selected and analysed using the two analysis techniques being studied, establishing the correlation between both. Table 1 lists the certified specific surface area of each reference material.

Sample	Certified value
Silica	0.18 ± 0.02
Alumina	5.4 ± 0.2
Titania	8.1 ± 0.3

Table 1. Certified specific surface area of the reference materials used in the study.

To validate the correlation method, different ceramic raw materials (quartz, kaolins, calcium carbonate, sodium feldspar, and zircon), as well as pigments and ferromagnetic ceramic materials used in manufacturing magnets, were analysed.

4. RESULTS

Initially, all the selected materials were characterised by both analysis techniques. Figure 4 shows the relationship between the direct parameters that can be determined by each technique, i.e. it plots the relationship between the specific surface area obtained by nitrogen adsorption versus the Sauter diameter, d_s , determined by laser diffraction, as it is the diameter related to the specific surface area of the material.

Figure 4 shows that the specific surface area decreased as the mean diameter of sample particle size increased, exhibiting an asymptotic trend for diameters above 10 μm . However, it may be noted that certain samples appeared to depart from the general pattern of behaviour. The samples at issue (clay, kaolin, pigment with high SSA, and two reference materials) displayed a common characteristic: they all exhibited a very high specific surface area with respect to their particle size. This behaviour could be due to two phenomena that had not been envisaged when it was attempted to relate the two analysis techniques at issue: particle shape and particle internal porosity. The laser diffraction method calculates all parameters assuming that the sample consists of spherical, solid particles, i.e. it is based on an ideal situation not always found in ceramic materials.

However, the gas adsorption method measures the real surface of the particles, adapting to irregular shapes and all types of apparent porosity.

In order to show the effect noted, different micrographs of the materials tested are shown in Figure 5. Materials are shown that displayed the general pattern of behaviour as well as materials that departed from this trend. As may be observed, the samples that exhibited the

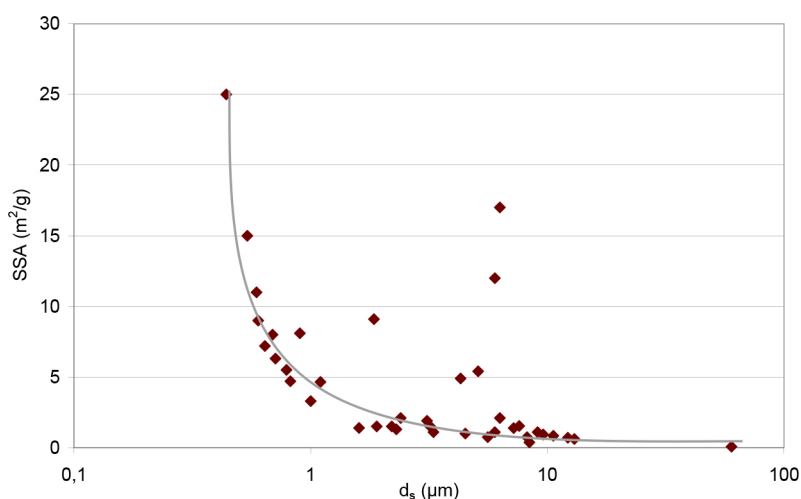


Figure 4. Relationship between the characteristic parameters SSA (m^2/g) and d_s (μm) obtained in each studied technique.

general pattern of behaviour, like the quartz or the pigments, had a particle shape with a higher sphericity index and lower internal porosity than the samples that departed from this trend, like the kaolin or the reference material. The kaolin, as well as the clay materials, which departed from the general pattern of behaviour, consisted of particles with plate-like structures, while the reference material had a very porous structure.

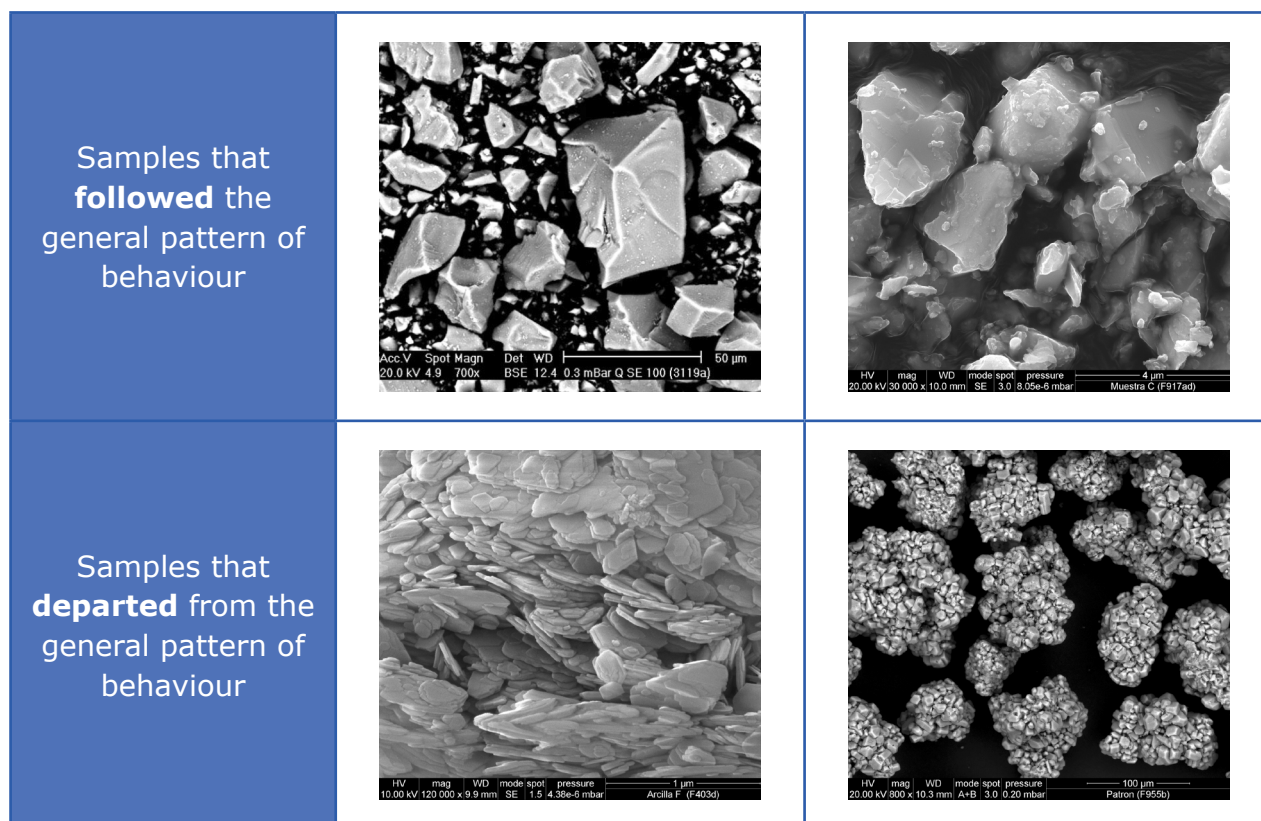


Figure 5. Micrographs of samples that followed the general pattern of behaviour (a-Quartz, b-Pigment) and samples that did not (c-Kaolin, d-Reference material).

Having established the intrinsic characteristics of the samples that allowed a good correlation to be obtained between the selected analysis techniques, the specific surface area values obtained from the Sauter mean diameter by the laser diffraction technique were calculated and plotted versus the values obtained by nitrogen adsorption.

Table 2 details the results obtained for each tested sample: SSA by nitrogen adsorption, d_{50} , d_s , and SSA by laser diffraction.

Type of sample	Sample	Gas adsorption	Laser diffraction		
		SSA (m ² /g)	d_{50} (μm)	d_s (μm)	SSA (m ² /g)
Reference materials	Glass spheres	0.07	63	60	0.04
	Silica	0.18	250	239	0.01
	α-Alumina	5.4	16	5.1	0.28
	Titania	8.1	1.11	0.9	0.94

Ceramic raw materials	Quartz SE-6	0.61	40	13	0.19
	Quartz SE-08	0.70	30	12.2	0.19
	Quartz SE-10	0.84	23	10.6	0.21
	Quartz SE-12	0.93	20	9.6	0.24
	Quartz SE-60	1.4	14	7.2	0.31
	Quartz SE-100	1.5	14	7.6	0.29
	Quartz SE-300	2.1	9.1	6.3	0.39
	Quartz SE-600	4.6	2.1	1.1	0.83
	Kaolin	12	8.0	6.0	0.33
	Clay	17	10.6	6.3	0.35
	CaCO ₃	0.74	7.5	5.6	0.44
	Sodium feldspar	1.1	15	9.1	0.25
	Zircon	1.1	16	6	0.22
	Alumina	4.9	10	4.3	1.26
Pigments	Pigment 1	1.5	3.6	3.2	0.40
	Pigment 2	0.38	11	8.4	0.15
	Pigment 3	1.9	3.8	3.1	0.50
	Pigment 4	1	7.0	4.5	0.23
	Pigment 5	1.5	2.2	1.9	0.20
	Pigment 6	9.1	2.5	1.85	0.76
	Pigment 7	1.3	2.5	2.3	0.56
	Pigment 8	1.5	2.5	2.2	0.56
	Pigment 9	0.74	10.1	8.2	0.16
	Pigment 10	1.1	5.8	3.3	0.37
	Pigment 11	1.4	2.1	1.6	0.81
	Pigment 12	4.7	1.04	0.82	1.38
	Pigment 13	2.1	2.9	2.4	0.49
	Pigment 14	3.3	1.21	1	1.3

Ferromagnetic ceramic materials	CEF 0h	5.5	0.94	0.79	1.4
	CEF 0,5h	6.3	0.83	0.71	1.6
	CEF 1,5h	7.2	0.74	0.64	1.7
	CEF 2,5h	8.0	0.71	0.69	1.6
	CEF 4h	9.0	0.68	0.60	1.9
	CEF 8h	11	0.64	0.59	1.9
	CEF 24h	15	0.58	0.54	2.0
	CEF 48h	25	0.49	0.24	4.6

Table 2. Characterisation of the test materials by the studied analysis techniques: SSA by nitrogen adsorption, d_{50} , d_g and SSA by laser diffraction.

Table 2 shows that, when the values obtained for the reference materials are compared, the laser diffraction technique was unsatisfactory for the determination of the specific surface area of samples with a high specific surface area because they had a porous inner structure. In contrast, the values obtained for these samples using the BET technique exhibited a good correlation with the certified values (Table 1).

It was subsequently evaluated for which materials there was a satisfactory correlation between the specific surface area data obtained by the two techniques (Figure 6). All the tested samples have been plotted in Figure 6a. In contrast, the samples that exhibited particle shapes with low sphericity and/or were porous were not plotted in Figure 6b, i.e. the samples that departed from the principle on which the laser diffraction technique is based.

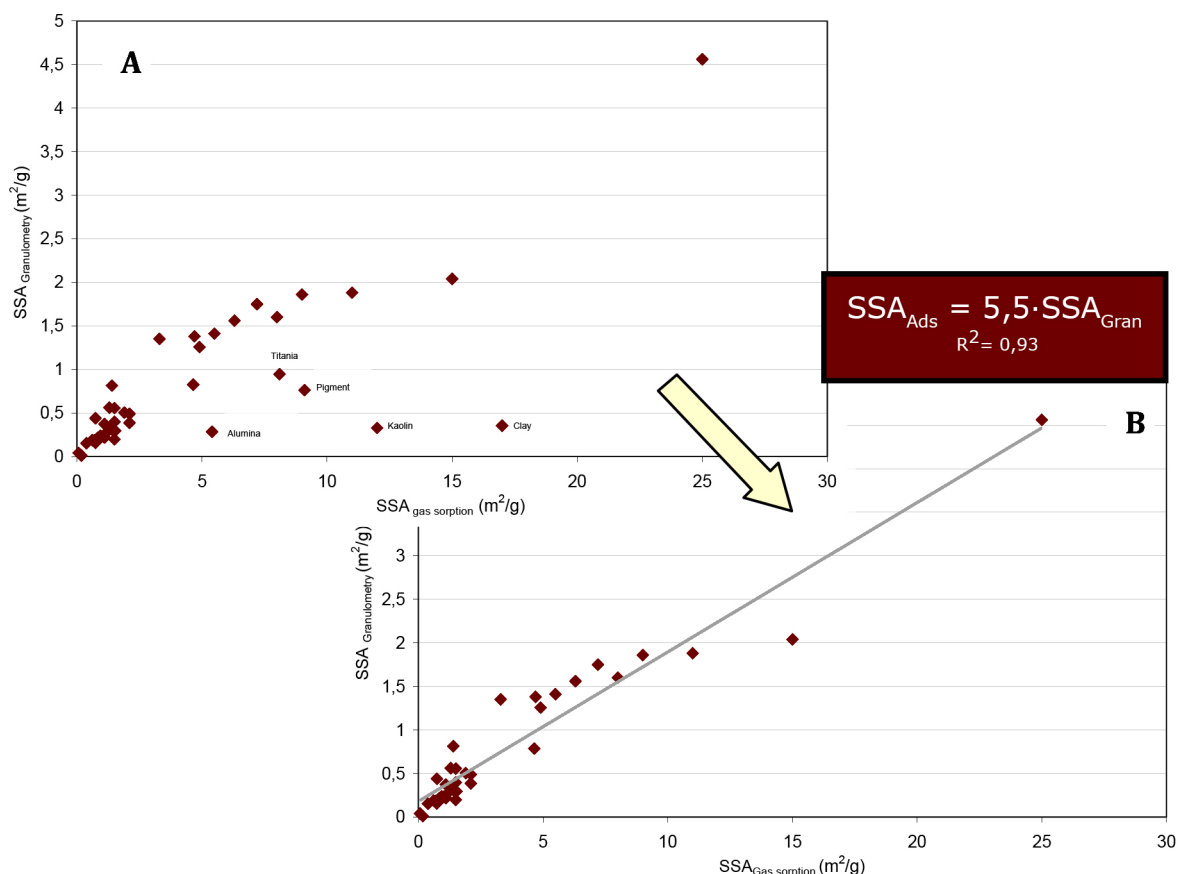


Figure 6. Relationship between the specific surface area values obtained by the two studied analytical techniques: gas adsorption and laser diffraction.

Figure 6 suggests that there was a linear trend for certain materials between the specific surface area obtained by both techniques, though the absolute values were not comparable. When a correction factor was calculated between both techniques, it was estimated that the specific surface area obtained by gas adsorption was approximately 6 times higher than that determined by laser diffraction. This correction factor was obtained on disregarding the values of the samples that did not follow the general trend discussed above (Figure 6b).

For each type of material, it was possible to determine a correction factor that provided values closer to those determined by the BET method. In this case, a new correlation by type of material was carried out, as shown in Figure 7, for the quartz samples and the ferromagnetic ceramic materials. The two materials exhibited different degrees of milling. Cases were selected with practically ideal structures because the type of sample had a pore-free internal structure and its shape was irregular, albeit with a certain degree of sphericity.

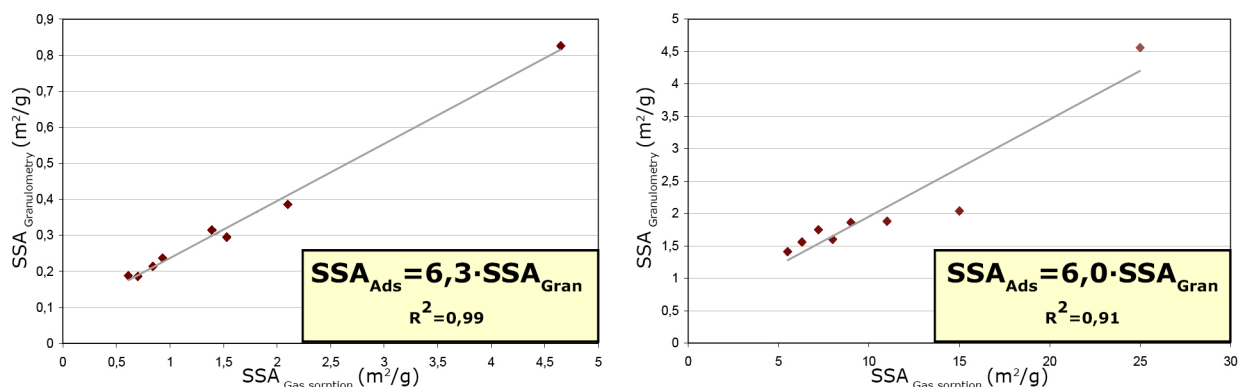


Figure 7. Relationship between the specific surface area obtained by the two studied analytical techniques, according to type of product: a) Quartz, b) Ferromagnetic ceramic materials.

The results obtained indicate that the families of ceramic materials displayed a similar trend to that observed in the general studied approach. However, the separation into type of material provided greater precision in the determination of the specific surface area of the material from the values of its particle size distribution and vice versa.

5. CONCLUSIONS

The specific surface area calculated by the two studied techniques was not comparable in absolute terms, the nitrogen adsorption technique being the technique that provided specific surface areas similar to the certified values. A possible linear relationship between the specific surface areas determined by the two techniques was estimated, such that the values obtained by the nitrogen adsorption technique were of the order of 6 times higher than those obtained by laser diffraction. The correction factor between both values depended on the type of material and was determined in a more precise way by separately studying each family of ceramic materials: for quartz, the correlation was 6.3; for ferromagnetic ceramic materials it was 6; and for pigments prepared by calcination with a low specific surface area it was 2.5.

Both techniques showed a good correlation with each other as long as the particles that were being analysed displayed high sphericity and/or practically zero porosity. This limitation was directly related to the measurement principle for wet laser diffraction, which relates the light scatter measured by the detectors with the diameters of totally spherical, solid particles, independently of their real shape and porous structure.

6. ACKNOWLEDGEMENTS

This project has been funded by the IVACE and FEDER funds under the Operational Programme ERDF 2007-2013 Valencia, through the aid of Registered Program established in the budgets of the Generalitat 2013 (PROMECE 2013).

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