METHODS OFGRANULOMETRICANALYSIS. APPLICATION IN THE GRANULOMETRY CONTROL OF RAW MATERIALS.

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ABSTRACT

The granulometric control of raw materials is fundamental in most ceramic processes, since it is directly related to the behaviour of the materials during the various stages of the manufacturing process and to the properties of the pieces produced. There are many techniques to determine granulometric distribution, all based on different physical principles and measuring different properties related to the particle size, such that the results obtained cannot be compared. When choosing a particular granulometric analysis technique, it is important to know the characteristic parameter which is measured, the range of sizes over which the technique is valid, and the reproducibility of the method, as well as additional information (density, refractive index) which is needed in order to obtain the granulometric distribution curve.

This report describes the existing techniques for determining particle size distribution, describing those which are most commonly used in the ceramic industry and the advantages and inconveniences which they present. At the same time, a comparison is made between the results obtained for natural and elaborated raw materials using different granulometric analysis methods: sedimentation and laser diffraction.

1. INTRODUCTION.

Controlling raw material particle size is of great importance in most processes which take place during the manufacture of ceramic products.

Particle size distribution, together with other characteristics such as shape and state of aggregation, determine the properties of the pieces produced (porosity, pore size, mechanical strength,...) and regulate the behaviour of various materials during the manufacturing process: permeability of the pieces to the passage of fluids, reactivity,... The determination of the granulometric distribution in raw materials is therefore of fundamental importance for the control and optimization of the manufacturing process as well as the properties of the finished articles.

Particle size measurement can be carried out using different procedures based on different physical principles (X-ray absorption, light diffraction, image analysis,...) so that the measurement depends not only on particles size but also on some of the properties of the material under analysis (density, refractive index,...).

The solid particles which constitute the raw ceramic materials come in a great many sizes and states of aggregation, and particle size measurement must be based on an ideal form, usually spherical, using different parameters to describe the particle size. These characterising parameters are usually based on the concept of the diameter of a circle or sphere which give a characteristic (volume, surface, speed of sedimentation, projected area,...) which is equivalent to the particle whose size is to be determined. Table I shows the most commonly used characterising parameters of particle size.

Symbol	Name	Definition
d_v	volume metric diameter	diameter of the sphere with the same volume as the particle.
d_s	surface diameter	diameter of the sphere with the same surface area as the particle.
d_t	sieve diameter	the equivalent size of the smallest square or round aperture through which the particle can pass.
d_{st}	Stokes diameter	diameter of the sphere with the same sedimentation velocity as the particle.
d_a	Projected area diameter	diameter of the circle with the same projected area as the particle

Table I

If all the particles of the characterised sample were spherical, the results obtained by the different techniques, and therefore with different characterising parameters, would be identical. However, in real systems the particles are rarely spherical, and in some cases can exhibit extreme irregularity. The more irregular the particles of the analyzed sample, the greater the difference between the granulometries obtained by different methods.

A powder sample is formed by many individual particles which have a continuous distribution of size and shape. The choice of the distribution function for a particular application is as important as the characterising parameter. Although the most common distributions are those of volume or mass (equivalent for a material of homogeneous density), area and number distribution are also used (Fig. 1.a.). These distributions can be either accumulated or frequency distributions: in the case of accumulated distributions, the total percentage of particles greater or smaller in size than a certain equivalent diameter is expressed; in the case of frequency distribution, the percentage of particles within a certain size interval is expressed (Fig. 1.b.).

1.1 Granulometric analysis techniques.

Granulometric analysis techniques are very varied, and record the particles' reaction to a certain physical phenomenon. The particle characteristics which are determined and related by size are the sedimentation velocity, dielectric properties, monochromatic light beam scattering, the permeability to air of a bed of the particles, the specific surface and, of course, direct measurements of the dimensions.

Table II shows the most common techniques of granulometric analysis, the physical phenomena on which they are based, the characterising parameter of size of the particle and the type of granulometric distribution. Also included are the size intervals in which they are valid and the advantages and inconveniences of some of the techniques.

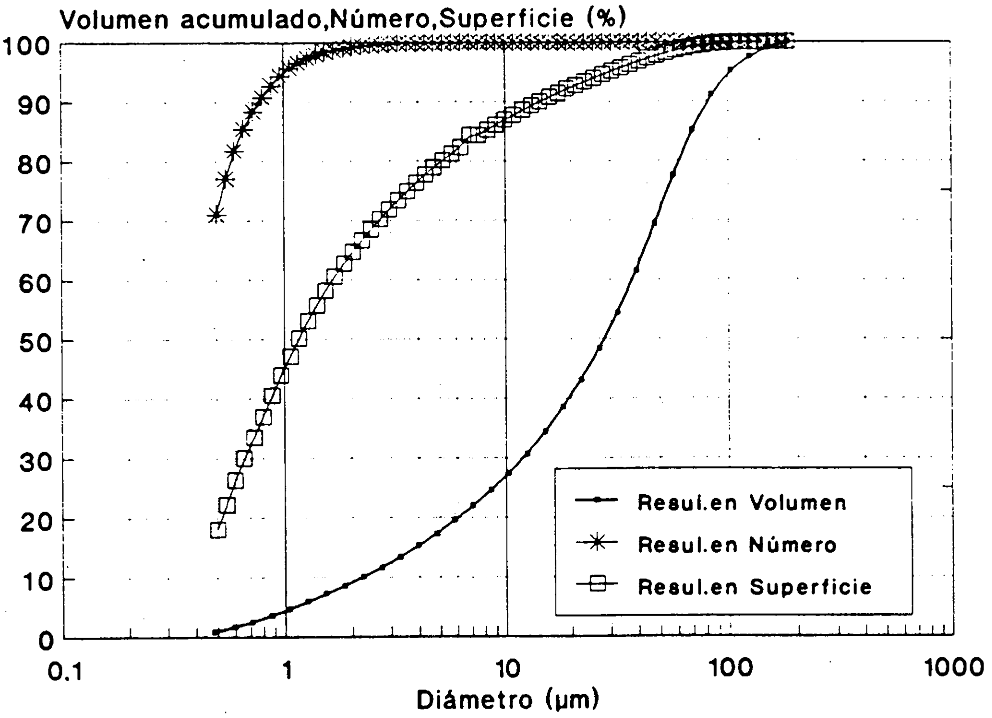

Figure 1.a. Accumulated distribution of volume, number and surface.

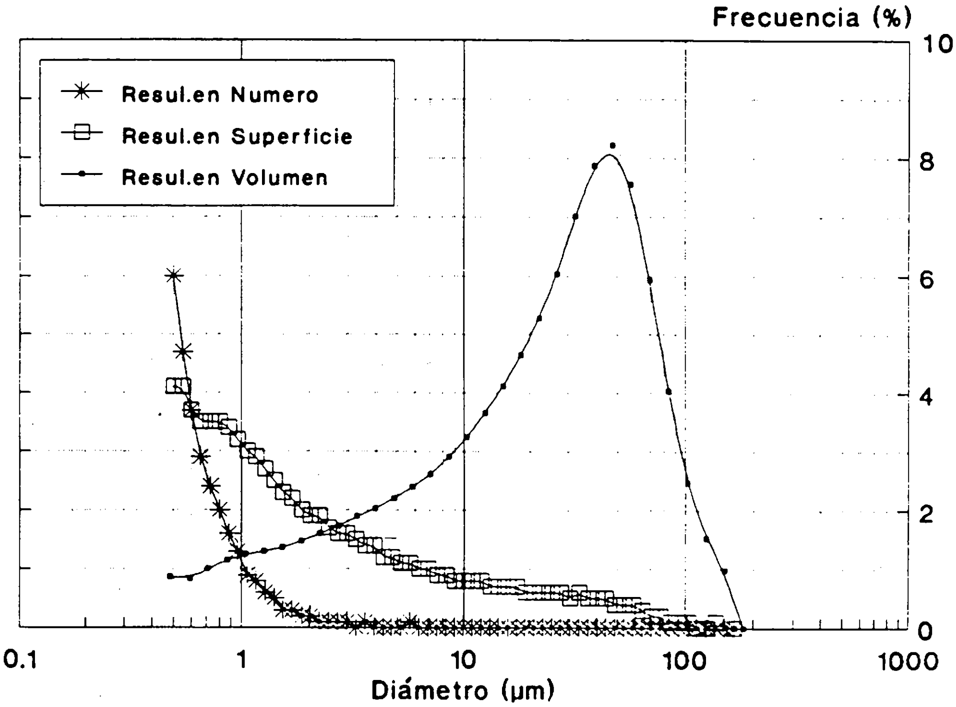

Figure 1.b. Differential distribution of volume, number and surface.

TABLE II

Método	Parámetro que se determina	Intervalo de aplicabilidad (μm)	Tipo de distribución	Inconvenientes
* Tamizado	diámetro de tamiz (sieve diameter), tamaño del cuadrado a través del cual pasa la partícula	4000-37	en masa	- Influencia del operador. - Normalización de telas. - Desgaste de las telas.
* Sedimentación	diámetro de la esfera que sedimenta a la misma velocidad que la partícula (diámetro de Stokes)	60-0.2	en masa	- Suponen partículas esféricas - Determinaciones en mezclas - Hay que conocer la densidad real
- centrifuga		30-0.02		
- pipeta Andreasen				- Ensayo muy largo
- absorción de rayos X		60-0.2		- Para elementos con N>13
* Contador Coulter	diámetro de la esfera que presenta el mismo volumen que la partícula	200-0.8	en volumen	- Para distribuciones anchas se requieren multiples aperturas - Interacción sólido-solución de electrolito
* Difracción de láser	diámetro medio de todas las áreas proyectadas de la partícula	300-0.1	en volumen	- Determinaciones en mezclas - Hay que conocer el índice de refracción - Asume partículas esféricas - Interacciones luz-partículas < 1 μm
* Microscopía (óptica o eléctronica) con análisis de imagen	diámetro del circulo con la misma área que la proyección de la partícula	>0.5	en número	- Se necesita medir gran número de partículas para que la determinación sea representativa

1.1.1 Methods of sedimentation. Sedigraph

The determination of the sedimentation velocity by X-ray absorption is based on Stokes' law for the free fall of particles in a viscous medium, the Lambert/Beer law for electromagnetic radiation absorption and on the relationships between incident radiation, transmitted radiation, and X-ray density (1) (2). The results are obtained as a percentage of accumulated mass as a function of the Stokes diameter.

Applying the Stokes equation means the assumption is made that the particles are spherical, rigid, and the surface smooth. It is also assumed that the terminal velocity of the particle is reached instantaneously and that it moves with no interference or interaction with other particles of the system, conditions which are only achieved in very dilute suspensions. At the same time, the real density of the solid and the density and viscosity of the suspending medium must be known. For a solid of a given density and for a liquid of certain density and viscosity, there is a maximum diameter which can be measured by this technique. For particles greater in size than this maximum diameter, the Stokes equation can not be applied, given that the rate of free fall of the particles is no longer laminar. Logically, by varying the properties of the liquid used, the measurable size interval can be modified.

1.1.2 Laser diffraction.

In this technique a beam of collimated monochromatic light is used which, when incident on the particles, produces scattering phenomena which can be interpreted based on the Fraunhofer diffraction theories and in some cases on the Mie scattering (3) (4). As in the case of sedimentation it is assumed that the particles are spherical. If the particle size is significantly greater than the wavelength of the incident light, Fraunhofer diffraction can be used to evaluate the particle size distribution. If the particle size is of the same order as the wave length of the incident light, the resulting scattering can be described by the Mie theory and the refractive index and the particle absorption have to be considered in order to interpret the data.

In the range of validity of the Mie theory, the technique is sensitive to the irregular morphology of the particles and to variations of the refractive index of complex samples consisting of mixtures of different materials.

The problem with this technique lies in the treatment of the results for the smaller sizes (normally less than 2 m) since, as has been mentioned above, it is not possible to use the Fraunhofer diffraction theory and the Mie application is very complex.

2. OBJECTIVE

In this study, the advantages and inconveniences of the two most commonly used granulometric analysis techniques are considered: X-ray absorption (Sedigraph) and laser diffraction. To this end, the sample preparation conditions which ensure good reliability and reproducibility of the results are studied. At the same time, the influence of the parameters which must be known in order to carry out the determination (real density and refractive index of the samplebe analyzed and of the suspending medium) are studied, as well as the cases in which it is critical to know these parameters precisely. Finally, the results obtained by the above techniques are compared for different raw materials and for a ceramic glaze.

3. MATERIALS AND PROCEDURES

3.1. Materials

The particle size distribution of three groups of materials were determined:

- plastic raw materials: a Villar clay, used in sandstone tiling compositions, and an english kaolin, which is used as a glaze additive, were characterised.

- non-plastic raw materials: the materials tested were quartz (with an SiO_2 proportion greater than 98%, obtained by the grinding of kaolinic sand), alumina (corundum) and micronized zircon.

- frits and glazes: three different types of frits were selected. Frit F-1 represents a lead-rich composition, while frits F-2 and F-3 correspond to compositions which are rich in titanium and zirconium respectively. A glaze composition was prepared starting with a frit (F-4) rich in boron, calcium and barium, to which was added the zircon and the kaolin characterised within the group of natural raw materials. In usual glaze compositions the proportion of these additives is very low (less than 10%) such that in order to study the influence of these components on the granulometric distribution results, a composition with 50% frit, 25% kaolin and 25% zircon was prepared

3.2 Experimental procedure

In order to determine granulometric distribution, two different techniques were used: measurement of sedimentation velocity by X-ray absorption and laser diffraction. The tests were carried out respectively with a Sedigraph 5000 ET from Micromeritics and with the Mastersizer from Malvern.

Prior to carrying out the determinations, the sample preparation was optimized. To do this, suspensions of the same sample in water were prepared, in which the concentration of added deflocculent, the time for which the suspension was subjected to ultrasonics, and the solid contents were modified.

Once these optimum conditions were determined, suspensions with three grammes of the sample were prepared, using a suspending medium of 25 ml of a solution of 1.8 g sodium hexametaphosphate (HMF) and 0.4 g of NA_2CO_3 in 1 litre of water. This solution was subjected to ultrasonics for 5 minutes and was left to stand for 24 hours to achieve a good particle dispersion. Afterwards, the suspension was subjected once again to ultrasonics for 5 minutes and was shook continuously whilst the determinations were carried out.

The real density of the samples, necessary for the sedimentation method, was determined with a helium pycnometer.

The refractive index of the frits was calculated from its chemical composition using the Appen equation (5). For the glaze it was assumed that this property was additive and was calculated as a function of the refractive indices and the percentages of frit, kaolin and zircon.

As was mentioned in paragraph 1.1.2, the refractive index is not the only parameter which is necessary in order to obtain the distribution (the Mie theory); it is also essential to know the absorption of the particles of the material being characterised in the infrared region.

The apparatus used for the determinations enables the Mie corrections to be applied, introducing a four figure number, referred to as the "presentation". The first two figures of this parameter correspond to the ratio between the refractive index of the material and that of the suspending medium (normally water) and the last two figures are related to the absorption. However it is not easy to determine the absorption values and so a qualitative value depending on the material composition is chosen.

4. RESULTS AND DISCUSSION.

4.1. Sample preparation.

In any method of particle size measurement it is not possible to obtain reliable and reproducible results if a representative sample is not available or if the particles are agglomerated or tend to agglomerate during the experiment. The first step in the preparation is to ensure that the full dispersion of the particles in the suspension.

To optimize the state of particle dispersion, various proportions of deflocculent in aqueous solution are added. By shaking and with the help of the deflocculents, particle agglomeration is eliminated and the individual particles are stabilized due to the increase in the electrostatic repulsive forces.

The application of ultrasonics facilitates the dispersion of the agglomerations, but sometimes can destroy particles or aggregated particles and alter the results.

Given that the two techniques used in the study require suspensions in which the particles are dispersed, the optimization of the sample preparation was verified only by determining the granulometric distribution by one of the techniques: X-ray absorption.

To determine the particle size distribution in the ceramic materials, the principle variables which affect the state of suspension are the deflocculent concentration and the time under ultrasonics.

Figures 2 and 3 show the granulometric distributions obtained for a quartz and a clay with different concentrations of deflocculent in suspension. Bearing in mind that in the technique used errors of up to 5% are considered acceptable, it can be concluded that for very dilute suspensions of the material tested the deflocculent concentration does not affect the state of agglomeration over the range of concentration tested. For this reason an intermediate value was taken as a suitable suspension: a solution of 1.8 grammes of HMF and 0.4 grammes of NA_2CO_3 in one litre of water.

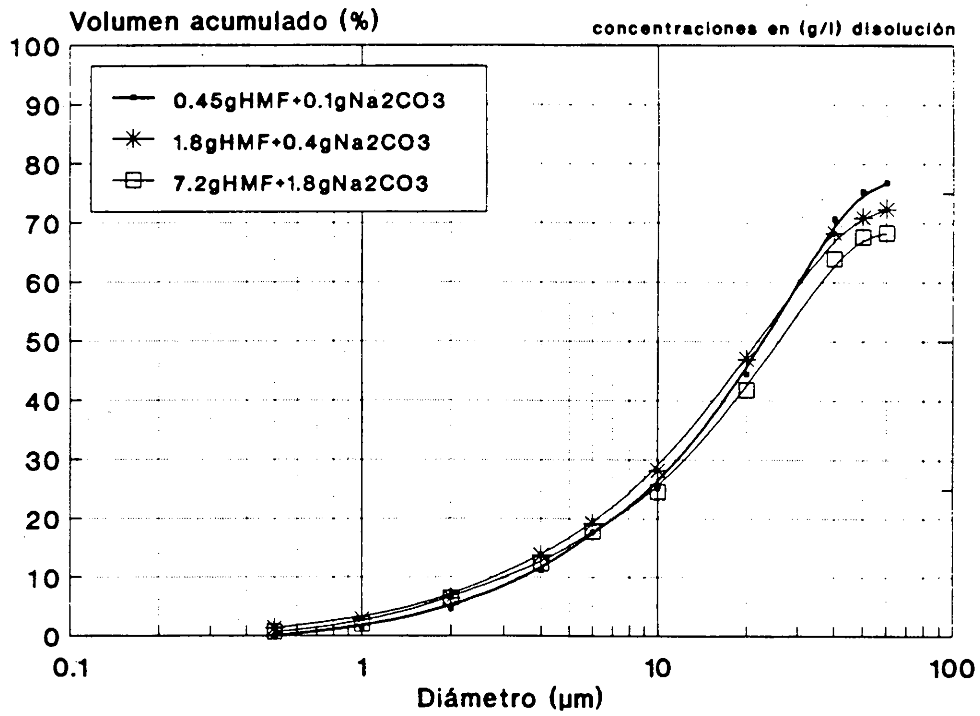

Figure 2. Effect of the deflocculent concentration. Sample: quartz

Figures 4 and 5 show the granulometric distributions of quartz and clay in the chosen solution, subjected to ultrasonics for different lengths of time. In the case of quartz (figure 4) there is hardly any difference between the curves. This is due to the fact that it consists of individual particles with little tendency to agglomerate and which do not fracture under the influence of the ultrasonics. However, for the clay, somewhat more significant differences between the different curves can be seen. The fact that the roughest granulometry corresponds to a determination carried out without using ultrasonics is explained due to the fact that the clay is a plastic material consisting of agglomerates. In order to eliminate them it is necessary to resort to mechanical means which enhance the action of the deflocculent. In fact, in the suspension subjected to ultrasonics for 5 minutes, the granulometric distribution obtained is considerably finer. For much longer periods, the curve hardly changes.

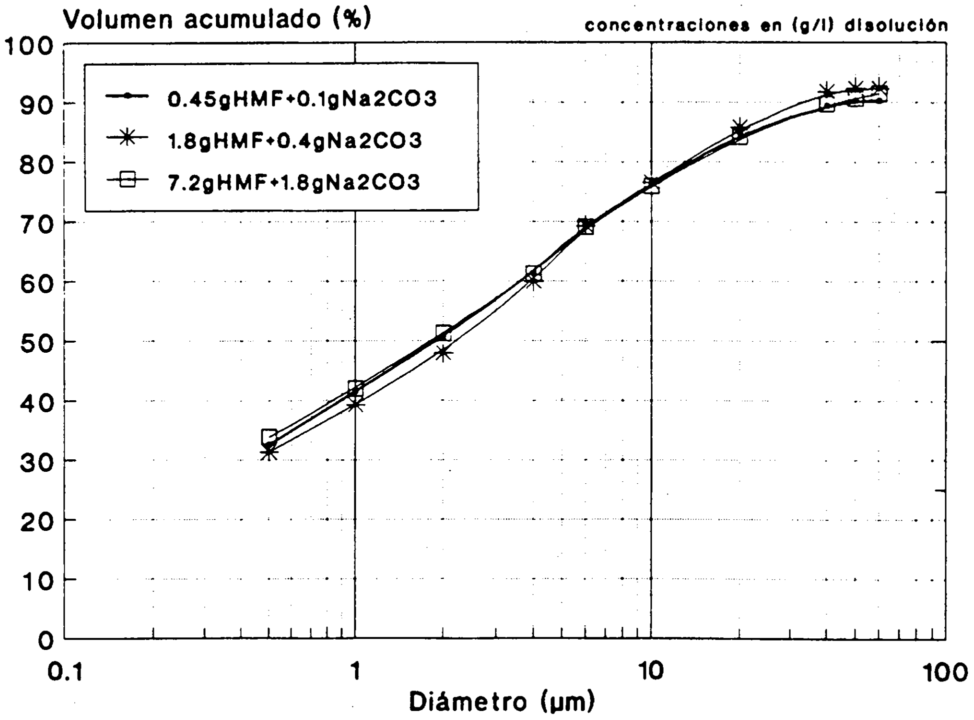

Figure 3. Effect of the deflocculent concentration. Sample: clay.

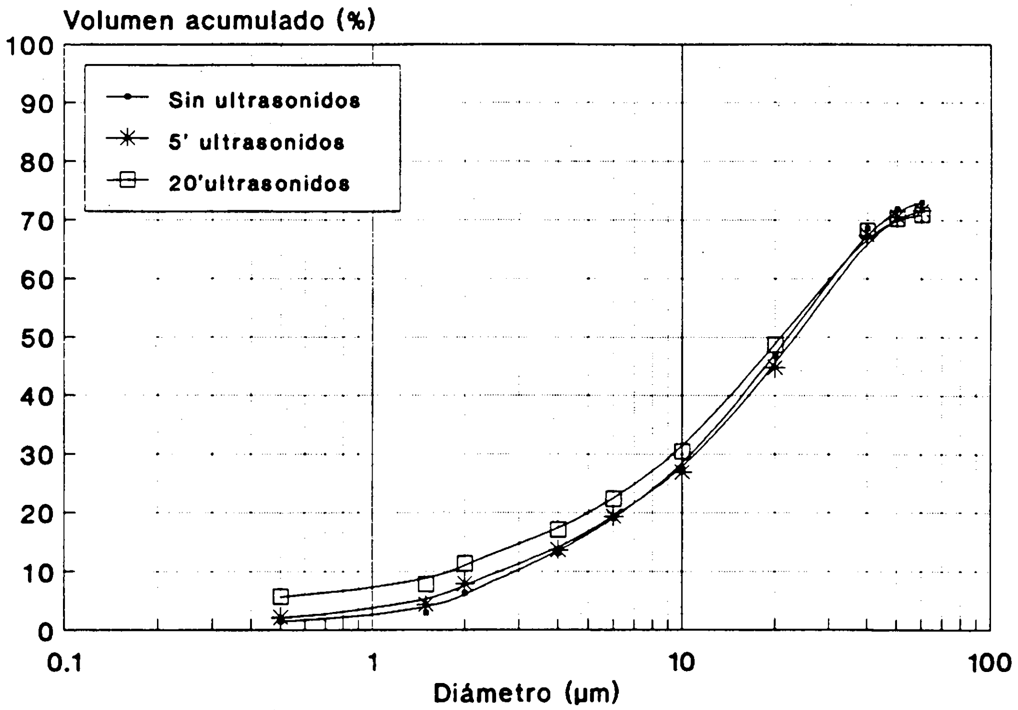

Figure 4. Effect of the time under ultrasonics. Sample: quartz.

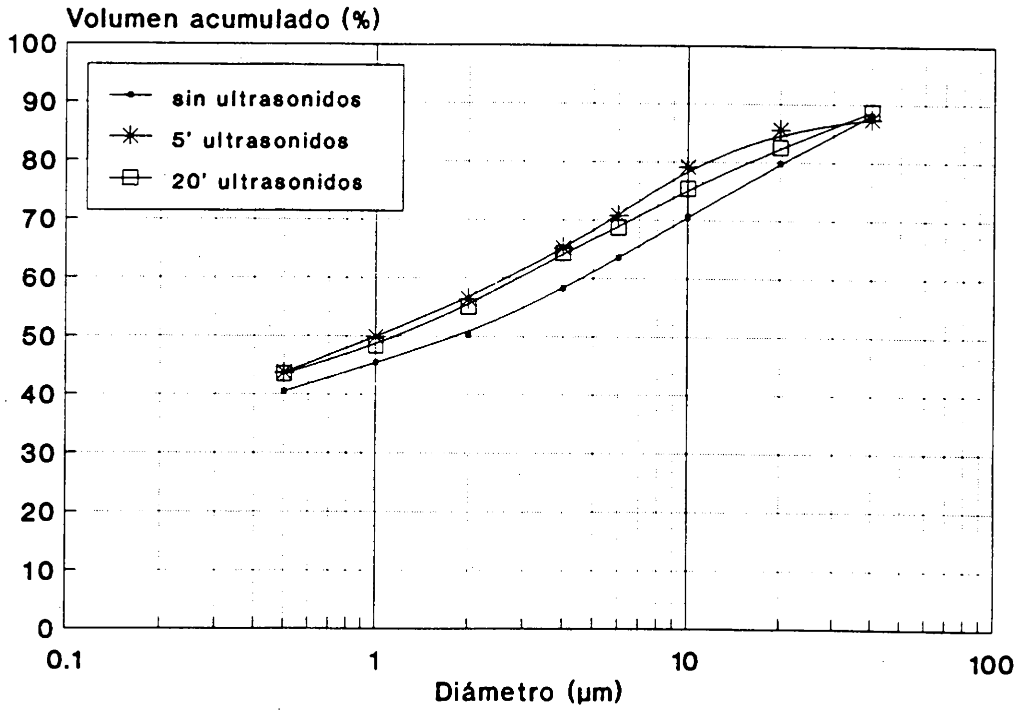

Figure 5. Effect of the time under ultrasonics. Sample: quartz.

As it can be appreciated, the particle size measurement is an absolute measurement, since by physical and chemical means it is possible to individualize the particles, to a greater or lesser extent, as a function of the type of material tested and the preparation process used, it being convenient to use standardised sample preparation procedures to be able to compare the results obtained from different determinations and/or from different laboratories for a given sample.

On the other hand, and only in the X-ray absorption technique, the addition of a deflocculent can have an effect on the results by modifying the X-ray absorption of the liquid medium. In this technique the first step in carrying out the test consists of measuring the X-ray absorption of the suspending medium in order to calculate the absorptionAccumulated volume (%) due to the particles alone. For this reason it is necessary that the deflocculent concentration in the "blank" solution is identical to the concentration in the suspension. In figure 6 it can be seen how the granulometric distribution results change for the same quartz sample (prepared in the conditions chosen as optimum) by using "blank" solutions with different deflocculent concentrations. As it can be seen, if the deflocculent concentration of the sample is less than that of the "blank" (curve 2 and 3), the proportion of fine particles is less than for the real sample (curve 1). The results obtained indicate the importance of this variable.

4.2. Granulometric distribution of non-plastic raw materials.

Figures 7 and 9 show the granulometric distributions for quartz, alumina and zircon determined by the laser and Sedigraph techniques.

For each of the materials tested the real density was determined experimentally and the corresponding "presentations" were calculated based on its refractive index and absorptions according to the description in section 3.2.. These values were later used to obtain the granulometric curves of these figures.

The great similarity between the results obtained by the laser and Sedigraph techniques for two different de-greasing materials can be seen, such that it can be deduced that both results are possibly very close to the real granulometric distribution of each sample.

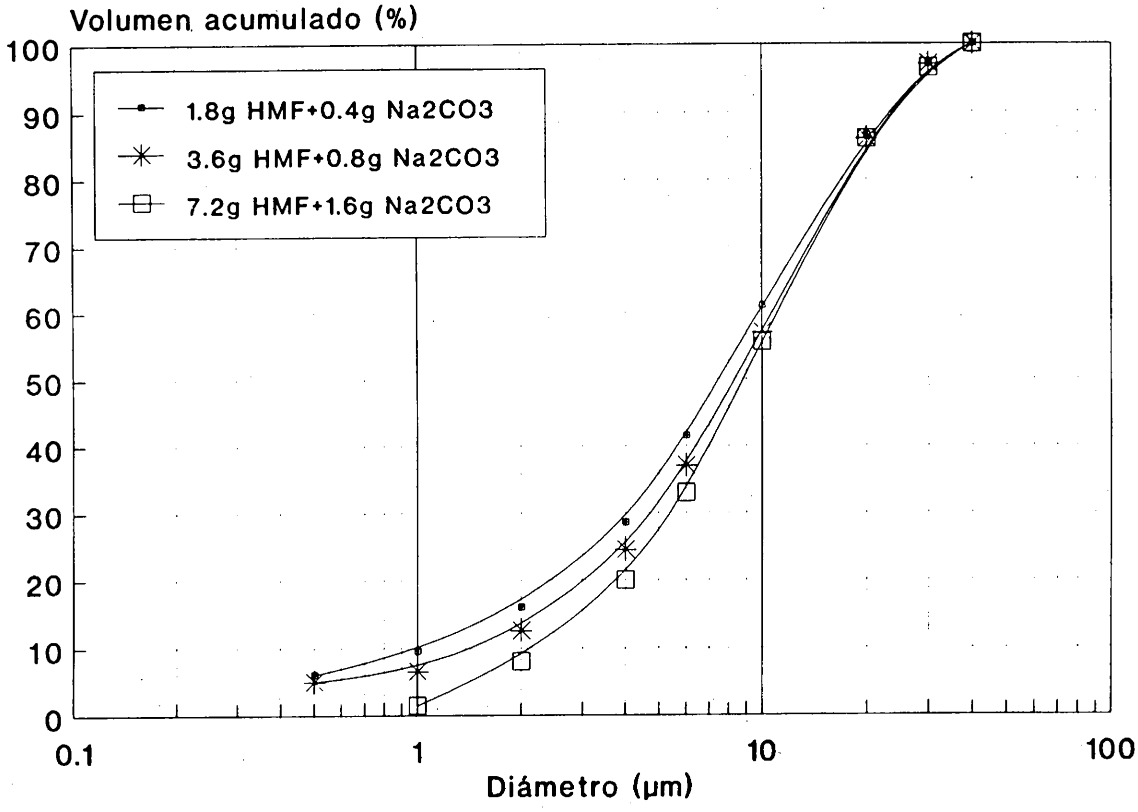

Figure 6. Effect of deflocculent concentration on the "blank" solution (g/l of solution).

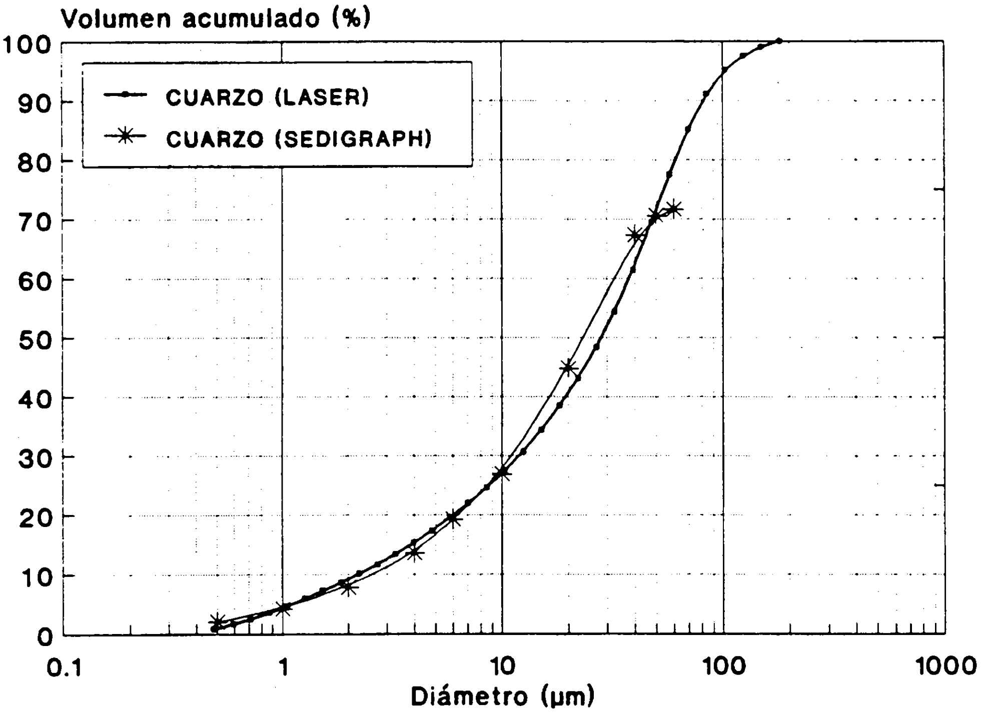

Figure 7. Comparison of the Sedigraph and laser results. Sample: quartz.

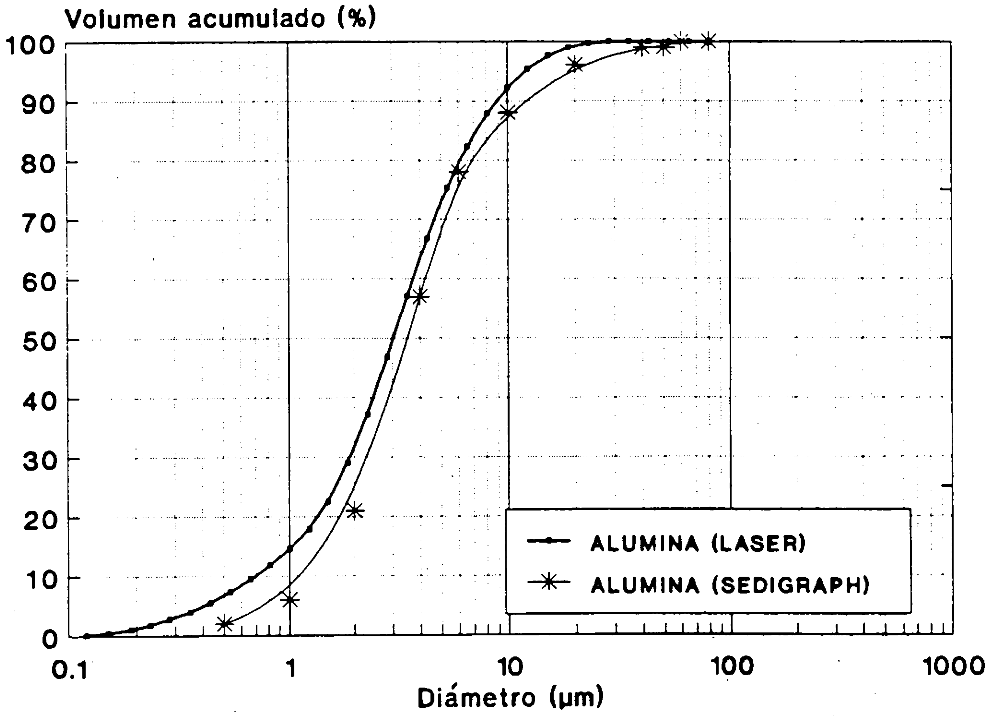

Figure 8. Comparison of the Sedigraph and laser results. Sample: alumina.

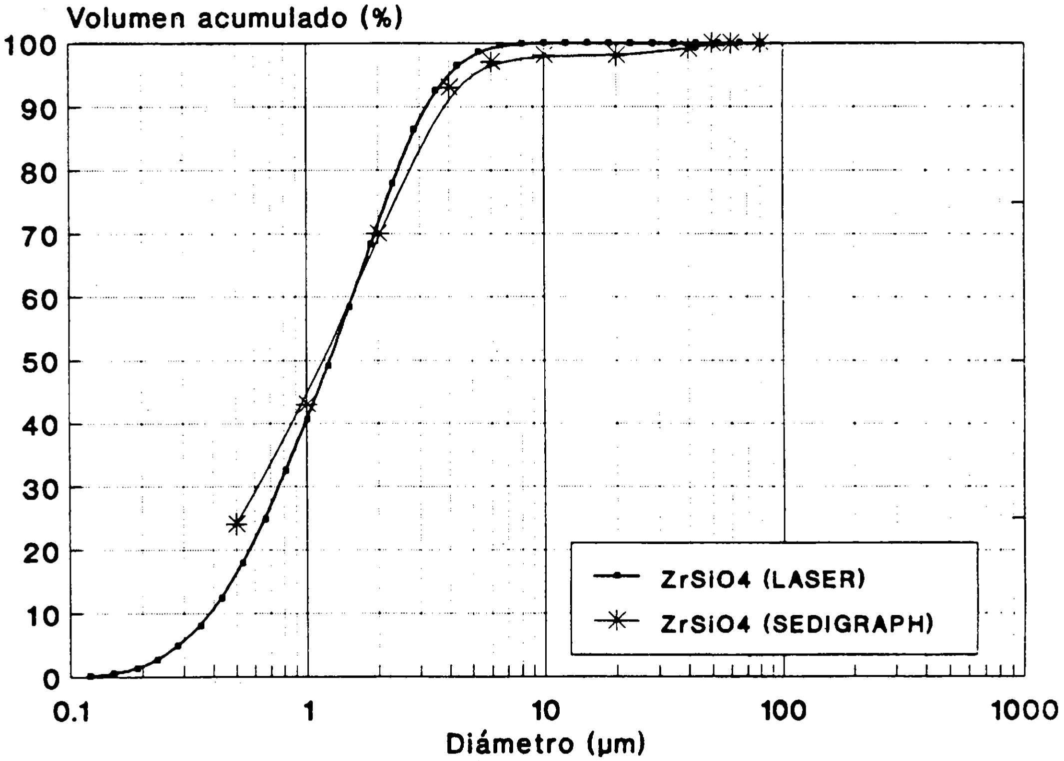

Figure 9. Comparison of the Sedigraph and laser results. Sample: zircon.

For these kinds of materials, the sedimentation and light scattering techniques seem to be equivalent, since the particles have shapes which are nearly spherical and do not form aggregates which are porous to any degree, and whose properties (density, refractive index, ...) would be difficult to determine.

In order to determine the effect of the refractive indices and the absorption in the laser technique for the tested materials, the results obtained for quartz with the presentation corresponding to its refractive index (0807=STND) and with the Fraunhofer presentation (FNHF) are shown. Figure 10 shows the results obtained. It can be seen that there are no significant errors due to choosing an unsuitable presentation. This is because the material has a rough granulometry and it is not necessary to apply the Mie corrections. However, in the case of ZrSiO4, which has a much finer granulometry, choosing the STND presentation or the corresponding one (1707) gives very different granulometric curve results (figure 11), since it is in the size interval where the Mie correction applies.

4.3 Granulometric distribution of plastic raw materials.

Figures 12 and 13 correspond to the particle size distribution determined by Sedigraph and laser diffraction for a kaolin and a clay.

As it can be seen, for this kind of material the granulometricAccumulated volume (%) distributions obtained by the two different methods differ considerably due to the laminar shape of the particles of which the samples consist. For kaolin, in which all the particles are laminar, the difference between the curves is greater.

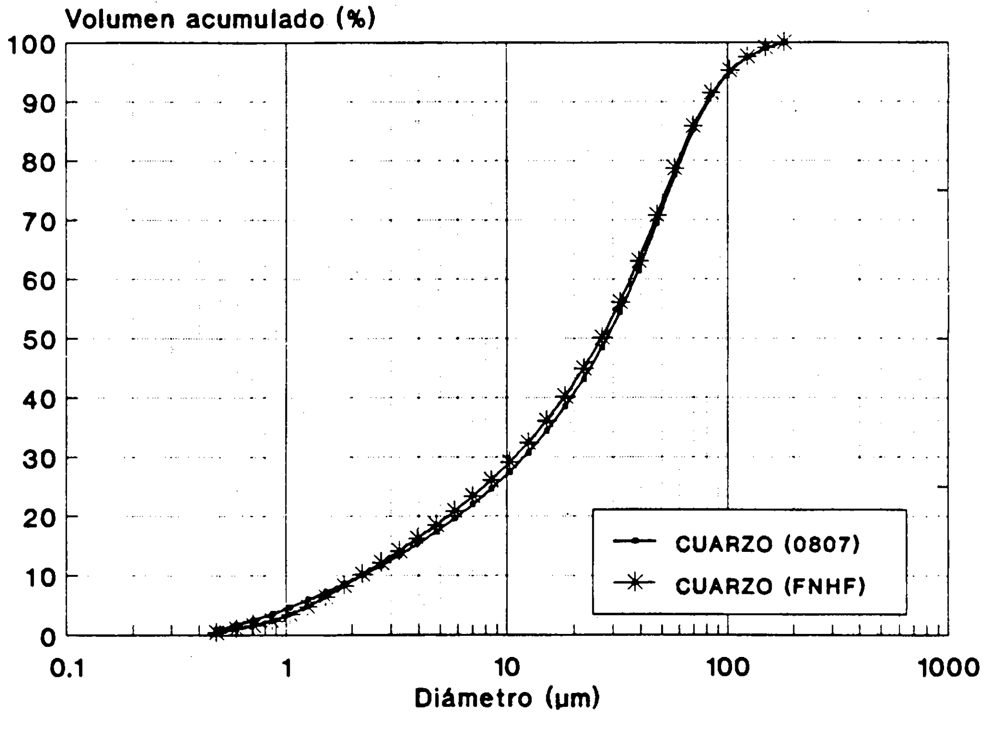

Figure 10. Effect of "presentation" value. Sample: quartz.

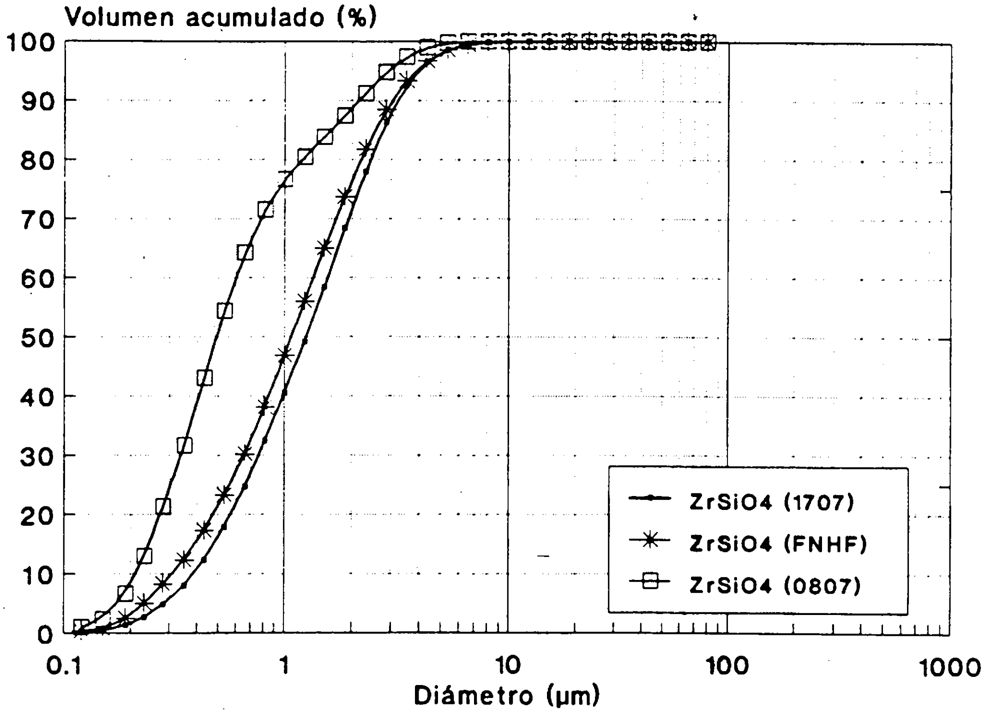

Figure 11. Effect of "presentation" value. Sample: zircon.

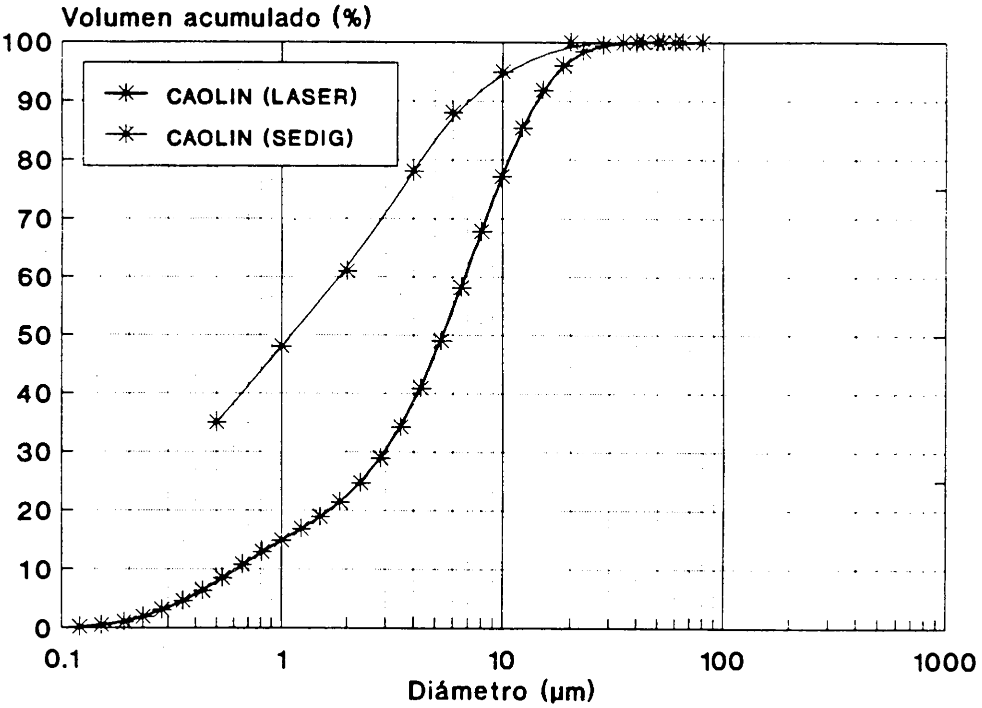

Figure 12. Comparison of the Sedigraph and laser results. Sample: kaolin.

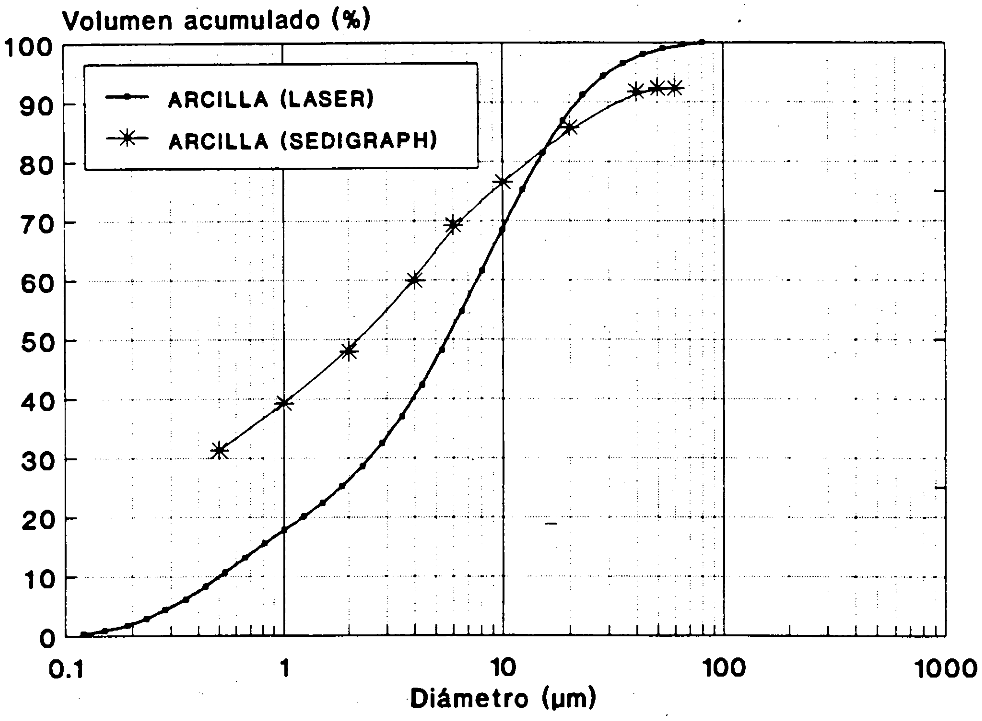

Figure 13. Comparison of the Sedigraph and laser results. Sample: clay.

These differences can be explained by the bases of the techniques used. Both methods assume that the particles are spherical, but a laminar particle undergoes sedimentation at a much lower velocity than a spherical particle of equivalent mass, such that the distribution obtained by the Sedigraph methods are much finer than the real distributions. In the case of laser there are also deviations from the real size distribution but since the particles cross the beam of light with all possible orientations, it can be expected that the granulometry obtained is closer to the real granulometry.

For the characterisation of clayey materials, sedimentation techniques are normally used (Andreasen pipette, Sedigraph), due to the possibility of predicting the plastic behaviour of these materials based on the particle size distributions obtained by this method, since the laminar particles behave as if they were finer than they actually are. With the Sedigraph method it is possible to distinguish a plastic material from a very fine degreasing material.

4.4 Granulometric distribution of frits.

In the previous paragraphs it has been shown that, for non-laminar particles, the results of the granulometric analysis carried out by Sedigraph and by laser diffraction are very similar, such that in principle it can be hoped that this will also be the case for frits. Nevertheless, these kinds of material have the inconvenience that both their refractive indices and their real density are not tabulated and one has to resort to experimental determinations or to estimations, knowing the chemical composition.

In order to establish the effect of these parameters upon the results obtained, three frits (paragraph 3.1) were chosen with different composition and therefore different densities and refractive indices.

The refractive indices of the three frits which were studied were calculated using the Appen formula (5) and the densities were determined experimentally, with the following results:

Frit	Refractive index	density (g/m^3)
F-1	1.772	4.76
F-2	1.558	2.45
F-3	1.584	2.84

4.4.1. Determinations by laser diffraction.

Figure 14 shows the granulometric distributions obtained for frit F-1 using three different presentations: standard (STND), Fraunhofer (FNHF) and 1409. The STND presentation is the one recommended for most materials or when the data for determining the value corresponding to the sample is not available. The FNHF presentation implies the use of Fraunhofer diffraction (without Mie corrections) in order to obtain thedistribution, which is correct for very rough granulometries or forhigh refractive indices and absorption values. Presentation 1409 was obtained from the calculated refractive index and assuming that this material has a high absorption since it is very rich in lead (about 60%).

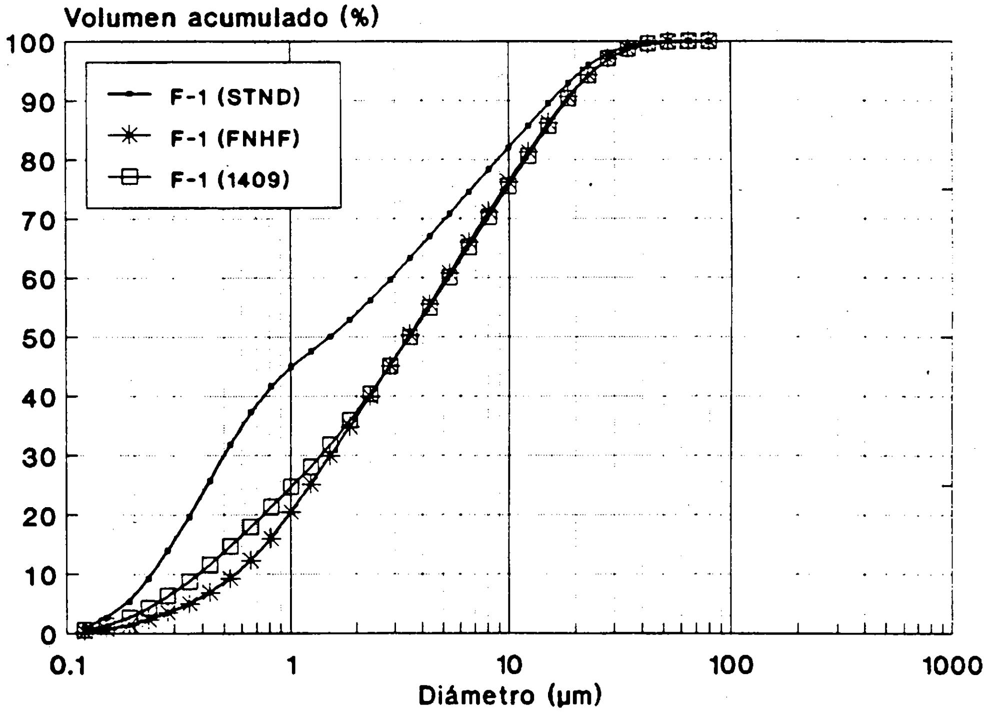

Figure 14. Effect of "presentation" value. Sample: frit F-1.

As can be seen, the presentation used affects considerably the results obtained. Taking into account the high absorption of the sample, the high refractive index, and that it is not a very fine granulometry, it can be expected that the FNHF presentation is adequate, and that in practice will not differ greatly from the 1409 presentation, which was calculated from the material properties.

Based on the refractive indices of the three frit samples and the approximate values of the absorption index, the following presentations were chosen:

Frit	Presentation
F-1	1409
F-2	standard (STND)
F-3	0907

4.4.2. Sedigraph determinations

Figure 15 shows the granulometric distributions obtained for frit F-1 using the correct density and an approximate value. Note that the curves are slightly different, but that the value of the density seems to be less critical than that of the presentation in the case of laser diffraction.

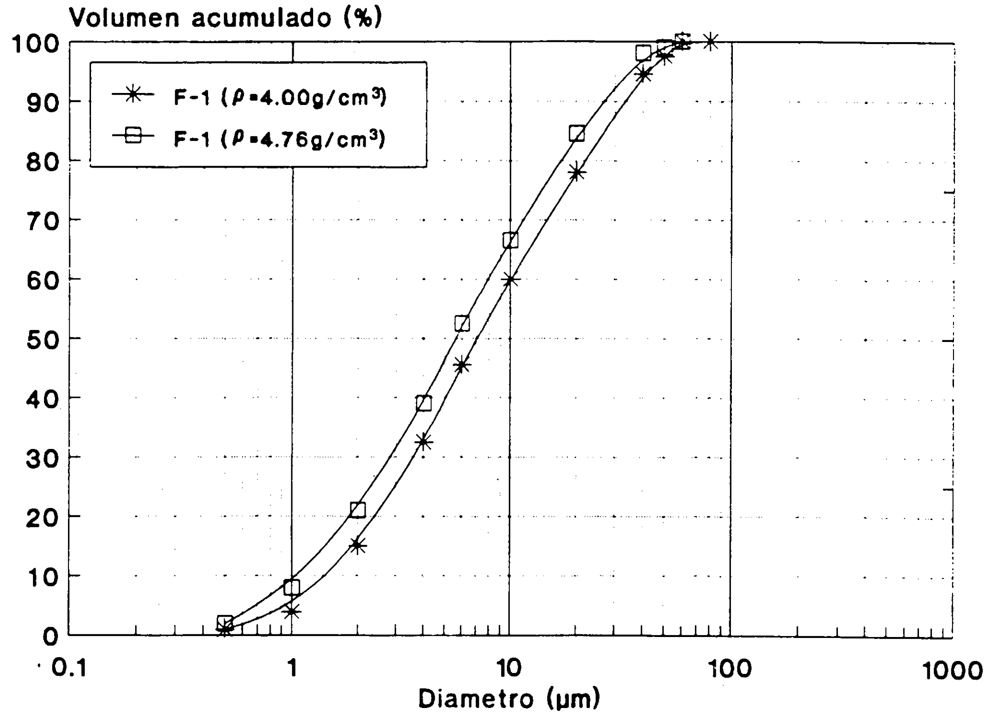

Figure 15. Effect of value of density. Sample: frit F-1.

When a density which is less than the real density is used, a rougher granulometric distribution is obtained, with a general displacement of the curve towards larger diameters. The average diameter changes but not the shape of the representations, which is what occurred by changing the presentation in the laser technique which was studied.

4.4.3. Comparison of the results of both techniques.

Figures 16 and 17 show the granulometric distributions obtained by the Sedigraph method (with experimentally determined densities) and by laser diffraction (with presentations corresponding to the calculated refractive indices) for frits F-2 and F-3.

The difference which is observed between the two curves for sample F-3 may be due to the fact that this was and opaque frit, rich in zirconium possibly present as zircon crystals. Since it is not a homogeneous glass, it can be hoped that the calculated refractive index differs from the real one.

The results obtained confirm that the Sedigraph and laser diffraction techniques for non-laminar particles are always similar if the parameters necessary for the determinations are known precisely.

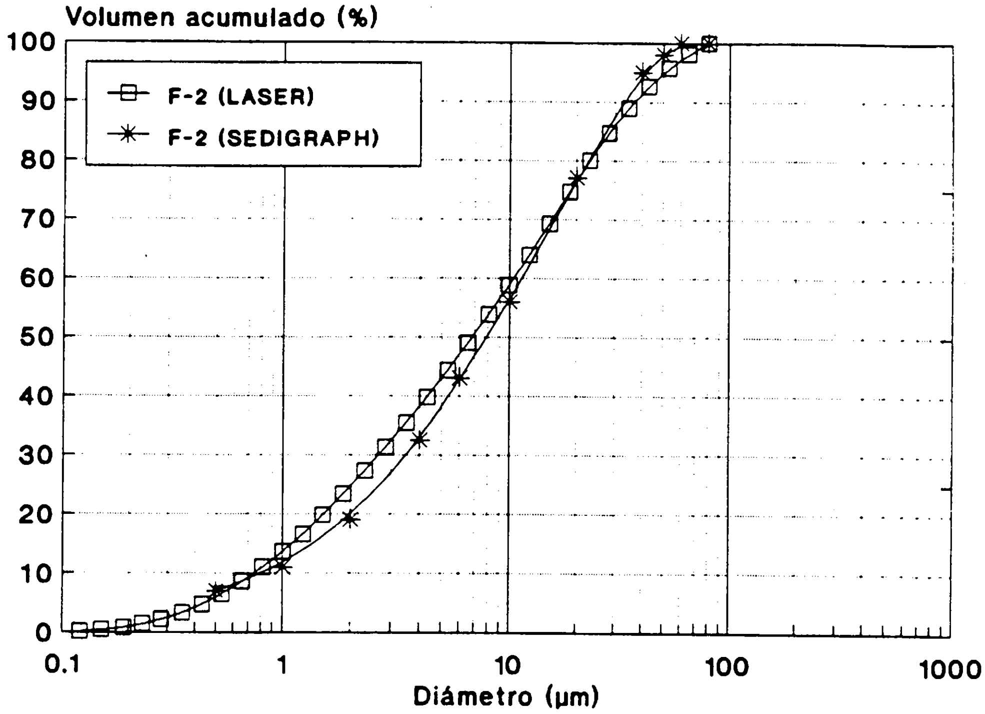

Figure 16. Comparison of the Sedigraph and laser results. Sample: frit F-2

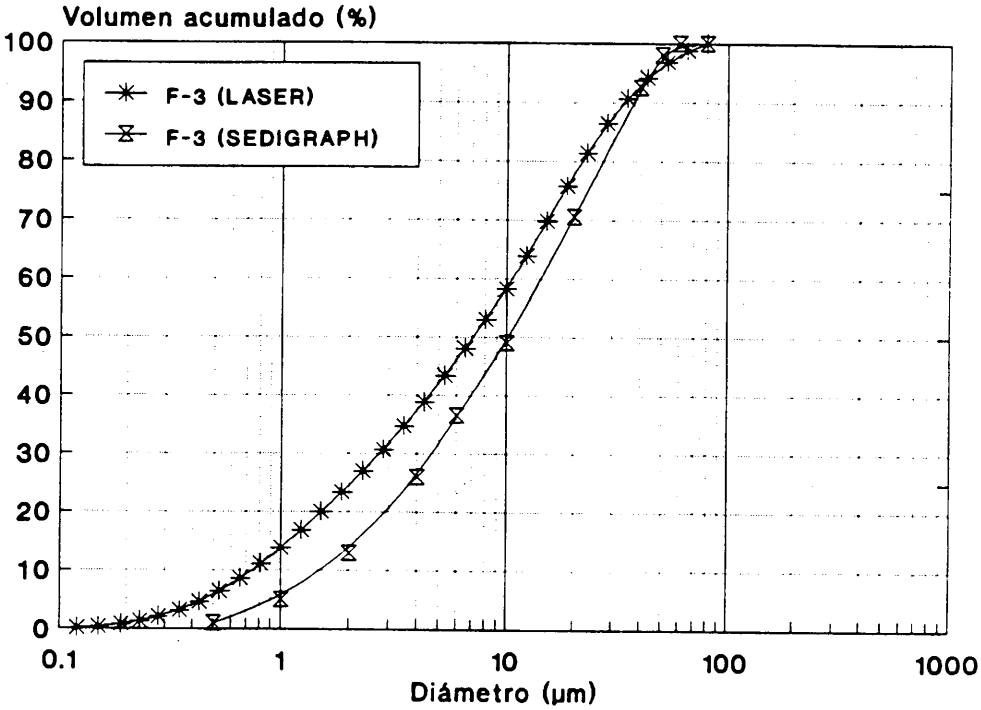

Figure 17. Comparison of the Sedigraph and laser results. Sample: frit F-3.

4.5. Granulometric distribution of a glaze.

As has been mentioned previously, the determination of particle size distribution of a mixture of materials is difficult since average values of density and refractive index have to be used, whereas in fact there are particles with different values of these parameters.

In order to determine whether the use of these average values is a good approximation, the granulometric distribution of a glaze was calculated based on the curves corresponding to each of the materials which constitute the mixture, and was compared with the curve obtained experimentally. These calculations were carried out for the case of laser diffraction and Sedigraph.

The refractive index of frit F-4, calculated by Appen for its chemical composition, is 1.56, so that the chosen presentation when carrying out the laser granulometry was 0807. The presentation which corresponds to the average refractive index calculated for the mixture is 0907.

In order to obtain the granulometric curve by the Sedigraph method, the real density of frit F-4 was determined, with the result of 2.51 g/cm^3. The average density used for the glaze was 3.07 g/cm^3.

Figures 18 and 19 show the comparison between the granulometric distributions of the three components which constitute the glaze, and the distribution calculated from the respective percentages by weight.

Figures 20 and 21 show the experimentally determined granulometric distributions next to the calculated ones for the two techniques studied. In neither case are there any significant differences. In the case of the Sedigraph method, the calculated curve is displaced towards slightly rougher sizes than that obtained experimentally. It can be hoped that the calculated curve is closer to the real curve, since it was determined based on the granulometric curves of the components. In figure 21, which corresponds to the laser granulometries, note that the difference between each curve is greater and that even the shape is altered. The curve obtained experimentally is narrower, although the average particle size is practically constant..

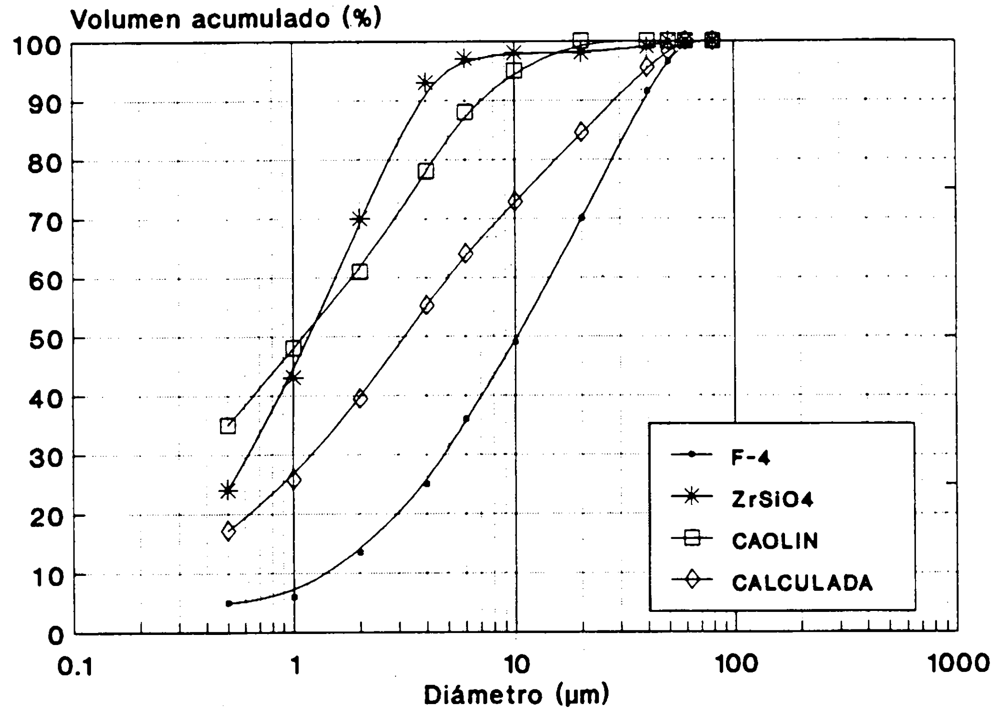

Figure 18. Sedigraph determinations.

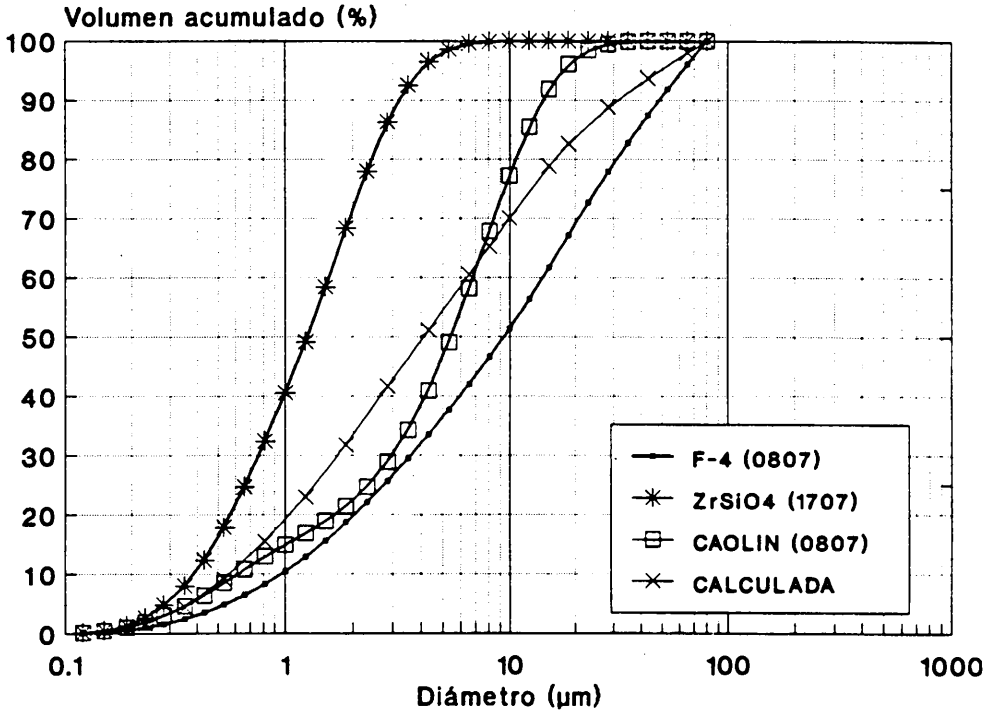

Figure 19. Laser diffraction determinations.

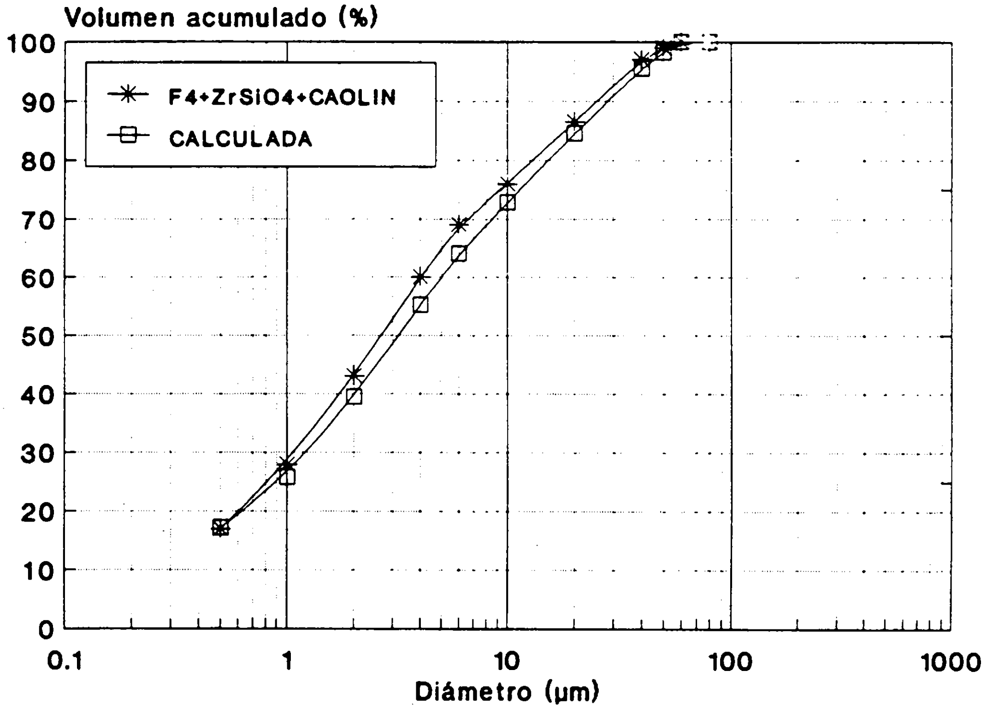

Figure 20. Comparison of the experimentally determined granulometric distribution and the calculated one based on the elements which constitute the glaze. Technique used: X-ray absorption (Sedigraph).

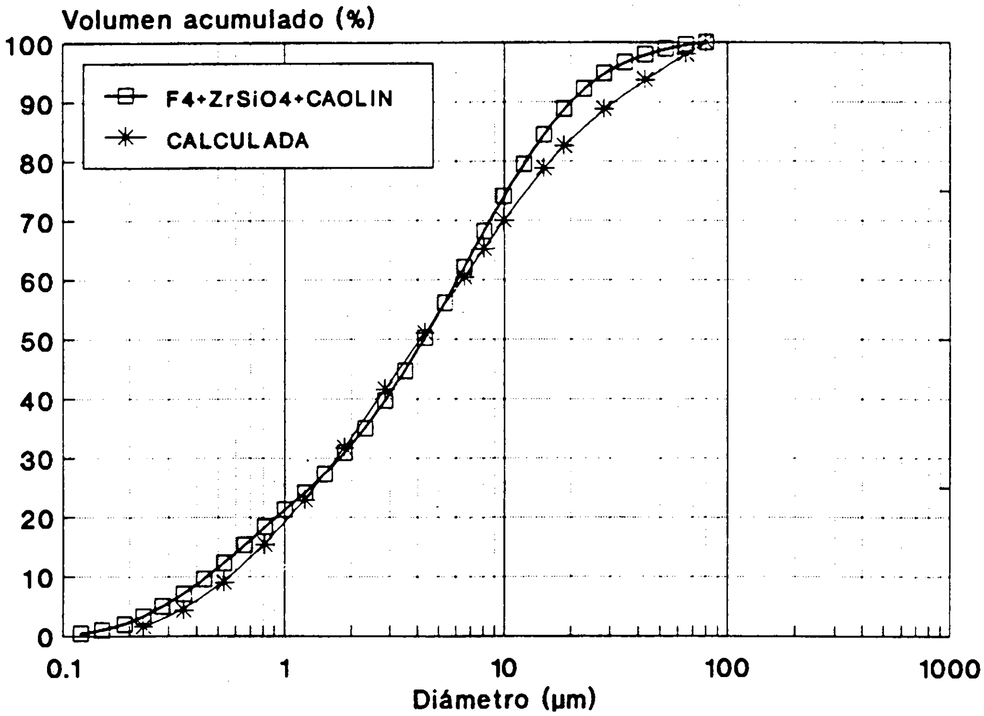

Figure 21. Comparison of the experimentally determined granulometric distribution and the calculated one based on the elements which constitute the glaze. Technique used: Laser diffraction.

5. CONCLUSIONS.

From the study carried out, the following conclusions can be drawn:

- In order to carry out granulometric analysis it is essential to have totally disperse suspensions. The sample preparation conditions determined in this study are valid for ceramic raw materials, however they are not valid in general. In order to control the granulometry of a raw material the sample preparation must be carried out in the same way so as to ensure good reproducibility of the results.

- For non-plastic raw materials it has been shown that the granulometric distributions obtained by laser diffraction are very similar to those obtained by the Sedigraph method, as long as the physical properties are known: density, absorption and refractive index.

- For clayey materials the results obtained by both techniques are notably different, since for these materials which consist of laminar particles, the sedimentation techniques give granulometric distributions which are finer than the real distributions.

- It is very important that the necessary parameters for calculating the granulometric distributions are available.It has been shown that for laser diffraction, in materials with a very fine granulometry, alterations in the refractive index lead to results which may differ greatly from reality.

- The absorption and refractive indices of frits vary considerably from some glasses to others, depending on the composition. When the composition of the sample is not known or the frit is not homogeneous, the results obtained by laser may be less precise than those obtained by Sedigraph, given that the determination of the real density is relatively simple. Despite this inconvenience, the great advantage of laser diffraction over the Sedigraph method is the speed and great reproducibility of the determinations, which is very useful for material control where the "presentation" can be considered constant for a given material.

- For glazes which consist of different materials, both the laser technique and sedimentation controlled by X-ray absorption, give results which are only approximate, given that average values of density and refractive and absorption indices have to be used.

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