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# WET PARTICLE CLASSIFICATION BELOW 1µm - CHALLENGE FOR BASIC RESEARCH AND TECHNICAL DEVELOPMENT

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## ABSTRACT

The dominating conventional processes of wet and dry classification in the particle range of more than 1µm are sieving and the different variants of stream classification. Approaching particle sizes of 1µm and below the conventional methods reach their present physical and technical limits. The economical relevance of particle systems below 1µm is permanently growing and thus a high demand on improved and new classification processes is existing. The grade efficiency, the selectivity and cost effectiveness of the methods used for such applications novadays are not satisfying or still not existing. In this paper the physical background of classification processes and the problems of fine particle classification will be described. The different physical principles and phenomena will be analyzed with regard to their potential for technical classification systems in the sub-µm range. Examples are given for promising techniques and ideas for new approaches.

## KEYWORDS

classification, fractionation, cut off size, grade efficiency, selectivity, nanoparticles

## 1. INTRODUCTION

The splitting of particle collectives into fractions of different particle size is a standard process in various technical applications. These standard techniques are until today mainly related to particle sizes of more than 1µm. They are based primarily on the principles of sieving and flow separation by counterflow or crossflow processes in the earth´s or a centrifugal field like schematically shown in fig.1.

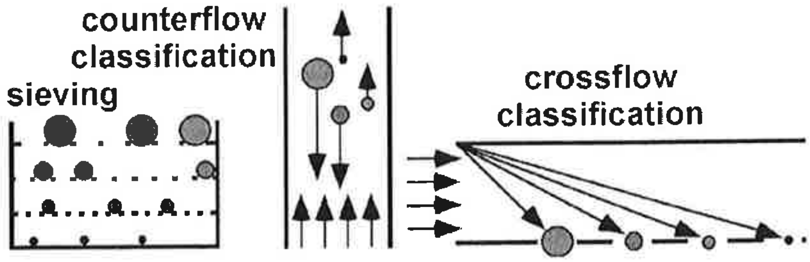


Fig.1: Sieving and flow separation for particle classification

Being influenced by competing forces particles of different size are transported to different locations in the sparation apparatus, collected and discharged there. The particles are dispersed either in liquid or gas. Due to the proceeding technical progress the application of dispersed solids in the µm or sub-µm and nanometer range is growing remarkably. This puts the also here necessary classification technology before completely new challenges. Many serious problems can arise, if particle size distributions are too broad. Exemplary for typical riscs of too coarse particles in the system should be named the impairment of the surface quality of paint films and coatings, the increased probability of defects during the CMC process (Chemical Mechanical Planarization) in the chip manufacturing, nozzle blockage while ink jet printing, reduced switching speed of ink jet printed circuits or decreased bio-availability of pharmaceutical active substances. Fig.2 gives an example for the time- and particle size dependend resorption of provitamin A in the blood of calves.

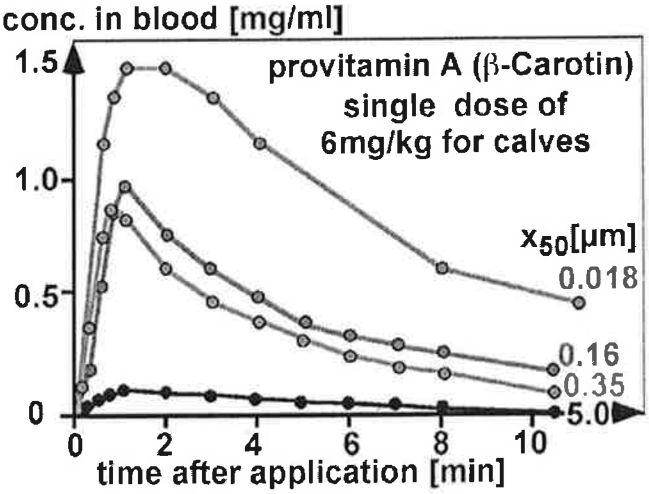


Fig.2: Bioavailability of provitamin A

An example of unwanted fine particles would be the less favourable separation of dispersed solid catalysts.

The necessity of having a well limited size fraction is given, if special optical effects should be realized and the particles must have diameters within the wave length spectrum for visible light of 400-800nm.

For purposes of particle size analysis in the nanoscale range some methods of particle classification like impactors or diffusion batteries are still existing for microscopic small amounts of material. On the other hand tasks of classifying within the sub-µm range for technical purposes are solved usually unsatisfactorily so far by sedimentation in special centrifuges or one-way depth filters. Numerous tasks of classifying are not considered as at all yet solved. Main cause for these difficulties are strongly decreasing mass forces with reducing particle size and in contrast to that substancially increasing surface forces. As a consequence attractive interactions between the particles can lead to agglomeration and they can be separated only hard or not at all according to their size. The stabilization of such particle systems is difficult in a gaseous atmosphere. In aqueous liquids particles can be stabilized more easily by adjusting the pH-value or limitation of the ionic strength. However this is often impossible due to functional-conditioned demands, as for instance additives and thwarted by mechanical influences like shear flows, which are generated for example by agitators or pumps.

## 2. DEFINITION OF TERMS AND SETTING OF TASKS

Particle classification exhibits beside sorting, separation and splitting one classical subsection of the unit operation separation in the field of mechanical process engineering.

Classification means the separation of a particle collective according to the geometric dispersity attribute size from a minimal particle size $x_{min}$ to a maximal particle size $x_{max}$ into a coarse and a fine fraction. The particle size at which the fractions are divided is called cut size $x_t$. Due to the fact, that an ideal technical or analytical classification is principally not possible, unfortunately some coarse particles will get into the fine fraction and vice versa. The grade efficiency function T(x) specifies for each particle size x of the feed material, which percentage is getting into the coarse fraction. The grade efficiency thus varies between 0 and 1 as can be seen from fig.3.

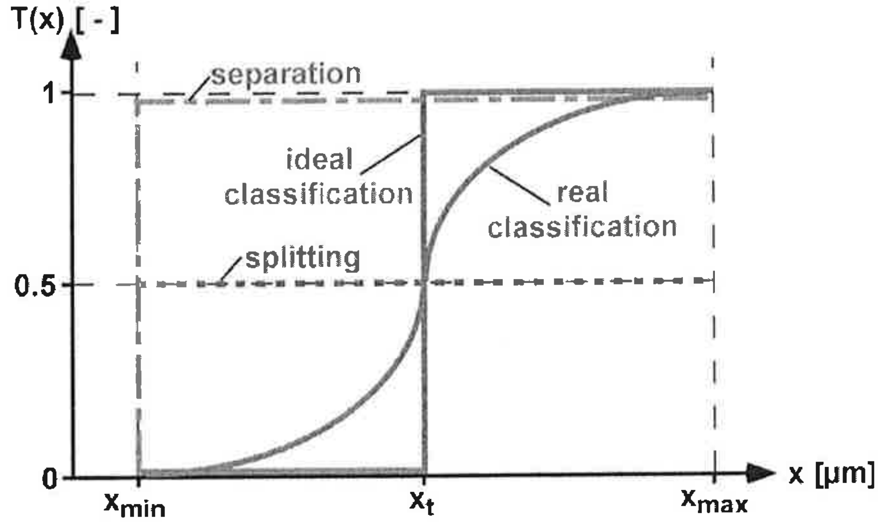


Fig.3: Grade efficiency function

The quality of a classification is the better the less particles are getting into the wrong fraction. For an ideal fractionation T(x) is a saltus function like to be seen in fig.3. The more T(x) deviates from the ideal curve, the les sharp the fractionation is. This can be characterized by the sharpness of the classification process.

Sorting means the separation of a particle collective according to any dispersity attribute than size like spec. weight, colour, shape or others.

Separation means the total separation of one phase from the other like solid liquid or solid gas separation.

Splitting means the separation of a particle collective into parts of same particle size distribution like practized for sample dividing before particle size analysis.

For the here relevant classification processes three main tasks can be defined, which can be distinguished systematically from each other:

- Removal of too coarse particles (degritting). This means, that for a certain cut size the largest particles of a monomodal material or peaks of a multimodal distribution, which can arise due to agglomeration of primary particles, have to be removed.
- Removal of too small particles (desliming). In this case the particle size distribution has to be cut off downwards from a certain particle size $x_t$.
- Narrowing of a particle spectrum into one or more size ranges (fractionating). In the ideal case a monodisperse material would be the result, but in reality a narrow

particle size distribution with well defined limits of allowed upper and lower particle size.

To be able to classify below a particle size of 1µm special difficulties have to be overcome in comparison to the coarse particle range.

- Due to the dominating surface forces in the here interesting particle size range it must be made sure, that the particles to be classified remain stable in the surrounding fluid (here liquid) and do not agglomerate under the influence of adhering forces.
- The success and quality of a classification process must be measurable quantitatively and precisely.
- The selected classification principle and process must be suited, to fabricate technically relevant amounts of product with a sufficient precise limited particle size distribution and reasonable costs.

## 3. ADHERING FORCES AS LIMITING FACTOR FOR FINE PARTICLE CLASSIFICATION

For particle sizes of less than about 100µm adhering forces likethe van-der-Waals force gain more and more influence and can lead to agglomeration, which hinders a classification process or makes it impossible. This is due to the fact, that the van-der-Waals force $F_{vdW}$ is growing linearly whereby the mass force $F_G$ grows with the third power of the particle diameter x:

$$F_{vdW} \propto \frac{A \cdot x}{a^2} \qquad (1)$$

$$F_G \propto x^3 \cdot \rho_S \cdot g \qquad (2)$$

A is the Hamaker constant, a the distance between the particles, $\rho_s$ the spec. solid weight and g the gravitational acceleration.

In principle the van-der-Waals force between particles is stronger in a gaseous environment than in liquids. This is one reason for the limitation of air classifyers to particle sizes of about 10µm, whereby wet classification gives more chances to get cut sizes below 1µm. The resulting Hamaker constant $A_{sLs}$ depends strongly on the combination of particles ($A_{ss}$) and surrounding fluid ($A_{LL}$ in the case of liquid). The resulting value $A_{sLs}$ is the greater the smaller $A_{LL}$ is in comparison to $A_{ss}$:

$$A_{sLs} \approx \left[\sqrt{A_{ss}} - \sqrt{A_{LL}}\right]^2 \qquad (3)$$

$A_{SLS}$= $A_{ss}$ means maximal adhesion in vacuum.

For fine particle classification special measures of dispersing must be undertaken to separate particles from each other. These may be mechanical forces generated for example by ultrasonic waves or a strong shear flow. Methods to stabilize particles are to mask the particles or to build up a repulsion potential by charging the particles electrostatically. For masking the surface the particles have to be covered by a substance ($A_{MM}$) , which leads to remarkable smaller resulting Hamaker constant $A_{MLM}$ than the pure solid surface $A_{sLs}$. An example is the masking of solids dispersed in water by xylol like to be shown in Fig.4.

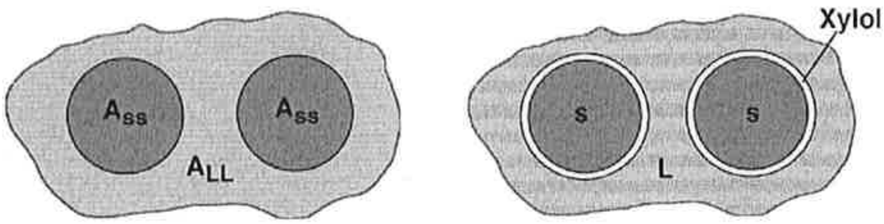


Fig.4: Masking of particles by xylol

The generation of a required repulsion potential can be realized by adjustment of the pH value or the ionic strength. Fig.5 shows the qualitative dependency of pH and ionic strength on the repulsive surface potential (Zeta-potential) of particles. The isoelectric point marks zero repulsion which means maximal attraction.

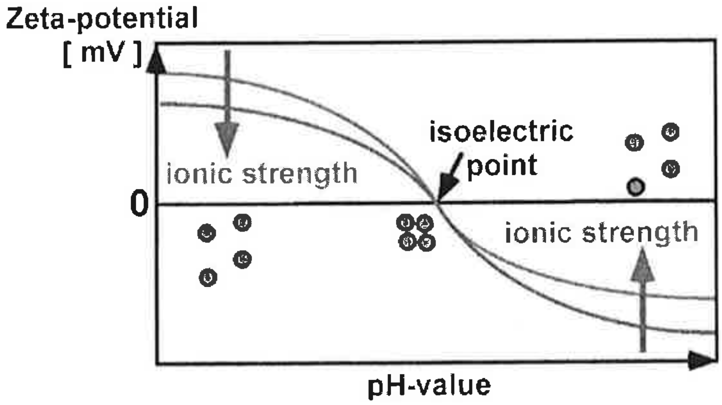


Fig.5: Influence of pH and ionic strength on the surface potential

Particles dispersed in polar liquids are influenced by attracting (van-der-Waals) and repulsive (electrostatic, Born) forces. Around particles, which are carrying an immobilized surface charge (Stern potential) a diffuse double-layer of counter ions is forming. The DLVO theory describes the resulting force balance like to be seen in fig.6.

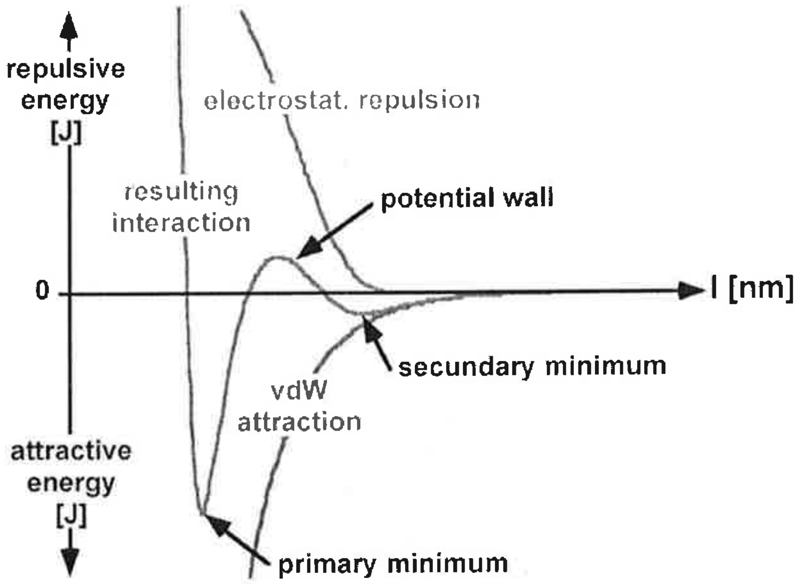


Fig.6: Adhesive and repulsive forces depending on the physico-chemistry

As can be seen from fig.6 the resulting potential wall has to be made high enough to hinder the particles from coming close enough to each other for sticking together. If particles are agglomerating in the secondary minimum, a mechanical dispersion can be realized relatively easy. If the particles are agglomerating in the primary minimum, a dispersion is very difficult. To overcome the repelling „energy-barrier“ the kinetic energy of the particles, which are moving relative to each other, must be high enough. Tab.1 illustrates a rough estimation of the interaction energy due to different mechanisms depending on the particle diameter.

| interaction energy in kT | particle 0.1µm | particle 1µm | particle 10µm |
|---|---|---|---|
| v.-d.-Waals attraction | ≈ 10 | ≈ 100 | ≈ 1000 |
| electrostatic repulsion | $0...10^2$ | $0...10^3$ | $0...10^4$ |
| repulsion by Brownean movement | 1 | 1 | 1 |
| kinetic energy due to sedimentation | $10^{-13}$ | $10^{-6}$ | 10 |
| kinetic energy due to stirring | ≈ 1 | $\approx 10^3$ | $\approx 10^6$ |

Tab.1: Interaction energy between particles of different size

These data illustrate, that for particles of 0.1µm shear forces by stirring are much smaller than pure v.-d.-Waals attraction. This means, that a mechanical desagglomeration in such a case is nearly impossible. On the other hand one can see, that in the case of enough kinetic energy the repulsive barrier can be overcome and an agglomeration takes place. As a result depending on the specific conditions a certain amount of kinetic energy can lead to agglomeration or desagglomeration. This kinetic energy can be generated by the shear flow in the feeding zone of solid bowl centrifuges, in the flow channels of dynamic cross-flow filters or by the action of stirrers or pumps. Depending on the locally acting kinetic energy the repulsive forces have to be made high enough to stabilize the particles. Unfortunately in several cases such an intervention into the physiochemistry is not allowed due to unwanted interaction with already present additives. In addition one have to take care for the stabilization of the particles not only before the classification to enable this process but also after the classification to preserve the required product properties. This is a difficulty in the case of drying a product after wet classification or the handling of electrostatically stabilized particles after a dry classification.

## 4. PROCESS CONTROL AND VALIDATION OF CLASSIFICATION RESULTS

A special challenge for the realization of classification processes in the sub-µm range will be the process control and the validation of classification results. There are some analytical methods available to measure particles in the range between 0.1µm and 1µm, but they normally are very high sophisticated, costly, time consuming and in some cases the danger of misinterpretation exists due to artefacts, which have to be identified and excluded from the results. Laser diffraction methods are approaching their lower limit at about 1µm. Small angle x-ray scattering is approaching its upper limit at about 0.1µm. Methods of using ultrasound need sufficient slurry concentrations, other techniques like dynamic light scattering (photon correlation spectroscopy - pcs) need high dilution of the sample and time. Especially the change of sample composition by dilution implicates the danger of particle destabilization and has to be managed carefully. Analytical disc centrifuges seem to be very well suited for the particle range from 0.1 to 1µm. They are operating offline today, need low particle concentrations in the sample and the time for one analysis takes only some minutes. Fig.7 shows the general principal of operation. The particle sedimentation in the centrifuge is stabilized by a slight density gradient within the liquid. The particles settle within an optically clear, roating disc. When particles are approaching the outer edge of the rotatng disc, they scatter a portion of a light beam that passes through the disc. The change of light intensity is continuously recorded and converted by the operating software into a particle size distribution.

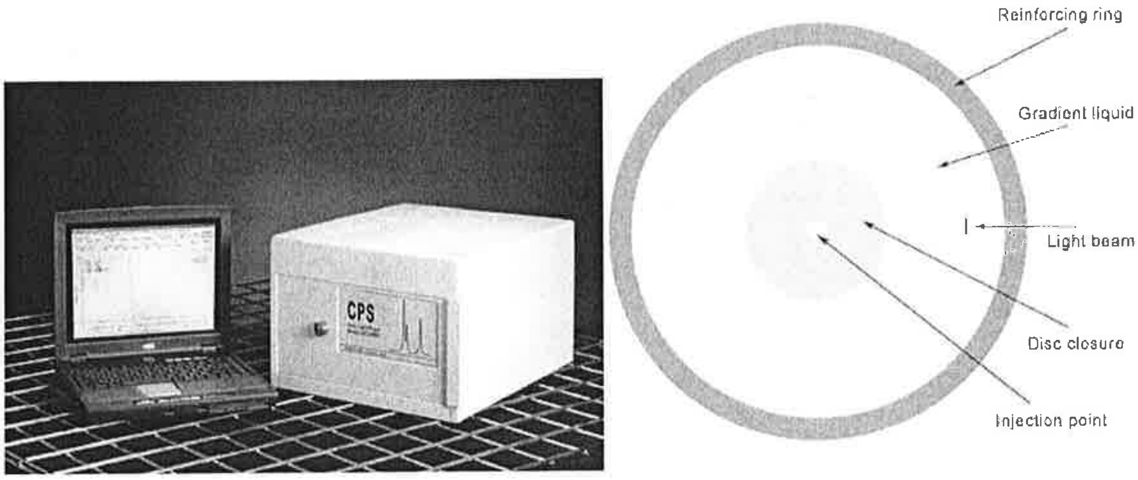


Fig.7: Front view of an analytical disc centrifuge (CPS Instruments)

In conclusion can be stated, that the particle size measurement for process control and product validation of industrial classification processes in the sub-µm range is principally possible but exhibits some open questions which have to be answered.

## 5. TECHNICAL CLASSIFICATION OF PARTICLES < 1µm

Today mainly two principles are used for technical classification of particles in the range from 0.1 to 1µm. According to fig.8 fibrous depth filters are representing one of these possibilities, which are especially used for the degritting of CMP slurries.

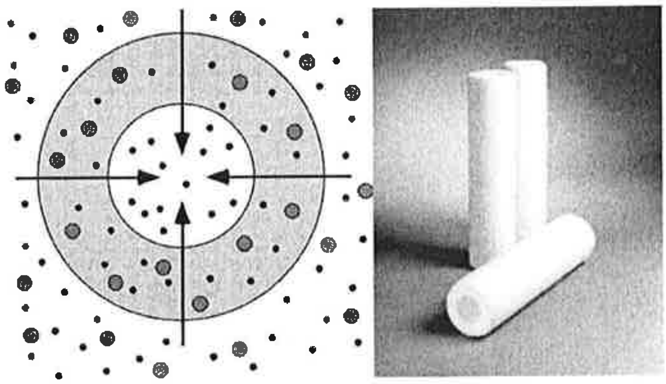

Fig.8: Depth filter to separate oversized particles from CMP slurries (Pall)

The oversized particles are separated safely in the structure of the filter whereby main part of the slurry can pass through. Unfortunately a remarkable amount of small particles is separated too. The filters are not regenerable.

The other principle is based on crossflow sedimentation in the centrifugal field. Especially tubular bowl centrifuges for very high accelerations of some 10000 x g like to be shown in fig.9 are well suited to fractionate sub-µm particles. Nevertheles the discontinuous operation and still insufficient sharpness of cut lead to the necessity of improving the principle and/or to look after new processes.

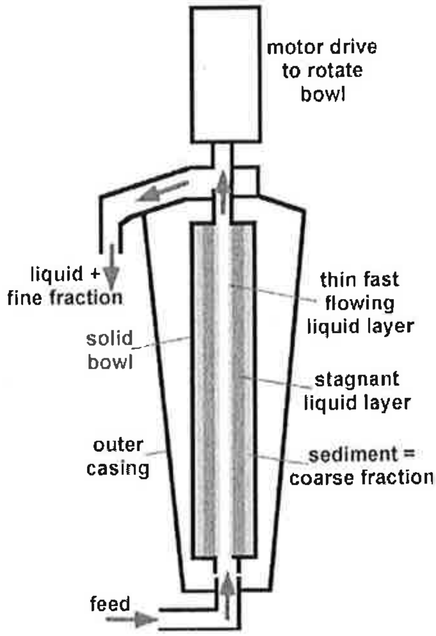


Fig.9: Tubular bowl centrifuge

One possibility of improvement could be the modification of centrifuges like disc stack separators to make the process continuous or to realize a cascade connection of centrifuges to improve the sharpness of cut. Other options could be to think about microporous membranes or improved methods of counterflow classification in the centrifugal field. Very interesting could be to check availabe analytical methods whether they could be modified to separate technical amounts of material. In every case there can be identified a strong need for progress in this field.

## 6. CONCLUSIONS AND OUTLOOK

Classification of particle sizes of more than 1µm can be judged as an industrially as far as possible solved problem and state of the art. However approaching particle sizes of 1µm and below classification is still a challenge and from many aspects only an unsuffient or still not solved task. The physically based problems for fractionation due to very small particle weight and strong particle interaction on the one hand, more and more applications for such materials on the other hand lead to the necessity of intensified research and development to offer improved and/or new classification techniques for the industry.

## 7. LITERATURE

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