

Suspension Stability

**Dietmar Lerche, Prof. Dr.
L.U.M. GmbH, Berlin, Germany**

**Convenor WG16 „Characterization of particle
dispersion in liquids”, ISO-TC24/SC4
„Particle characterization including sieving“**

Webster`s Dictionary:

1. The **Quality** of being **free from change or variation**
(at least for a given time > demixing or separation stability, shelf life)
2. The **Quality** or attribute of **being stable**
(to resist to a force > structural stability)

Scope:

..... that will address the characterization of stability of particles dispersed in a liquid for applications in new product design, optimization of existing products, quality control during processing, and product usage.

The stability of a dispersion is defined in terms of the change in one or more physical or physico-chemical properties over a given time period.

Stability, that means no changes of relevant product specifications and product performance, is important in industry and for end-users.

There are different wordings introduced reflecting different phenomena as well as views.

In the literature we find:

Dispersion, suspension or emulsion stability,
demixing or separation stability,
sedimentation or creaming stability,
physical stability,
colloidal stability,
kinetic stability,

The technical report does not cover phenomena which are induced by external factors, e.g. by radiation, by chemical or enzymatic reactions or are related to the growth/metabolism of biological organisms like bacteria.

These phenomena are often described as

photo, UV or irradiation stability,
thermal or chemical stability of one or the other constituent,
corrosion stability,
enzymatic or microbial stability,
etc.

As you see, we are between the devil and the blue sea:

There is no single physical or physico-chemical quantity, which serves as **the measurand** for the state of stability, means, which we have to measure.

In contrast:

There is a bunch of more or less defined quantities and there is often a confusion between stability related quantities and the stability behaviour of a dispersion

- So what to say about **Metrology** ????
- So what to say about **Measurand** ????
- So what to say about **Uncertainty** ????
- So what to say about **Traceability** ????

An analogy may help to clear the situation we are facing

Dispersion stability has similarities with the health status of a person.

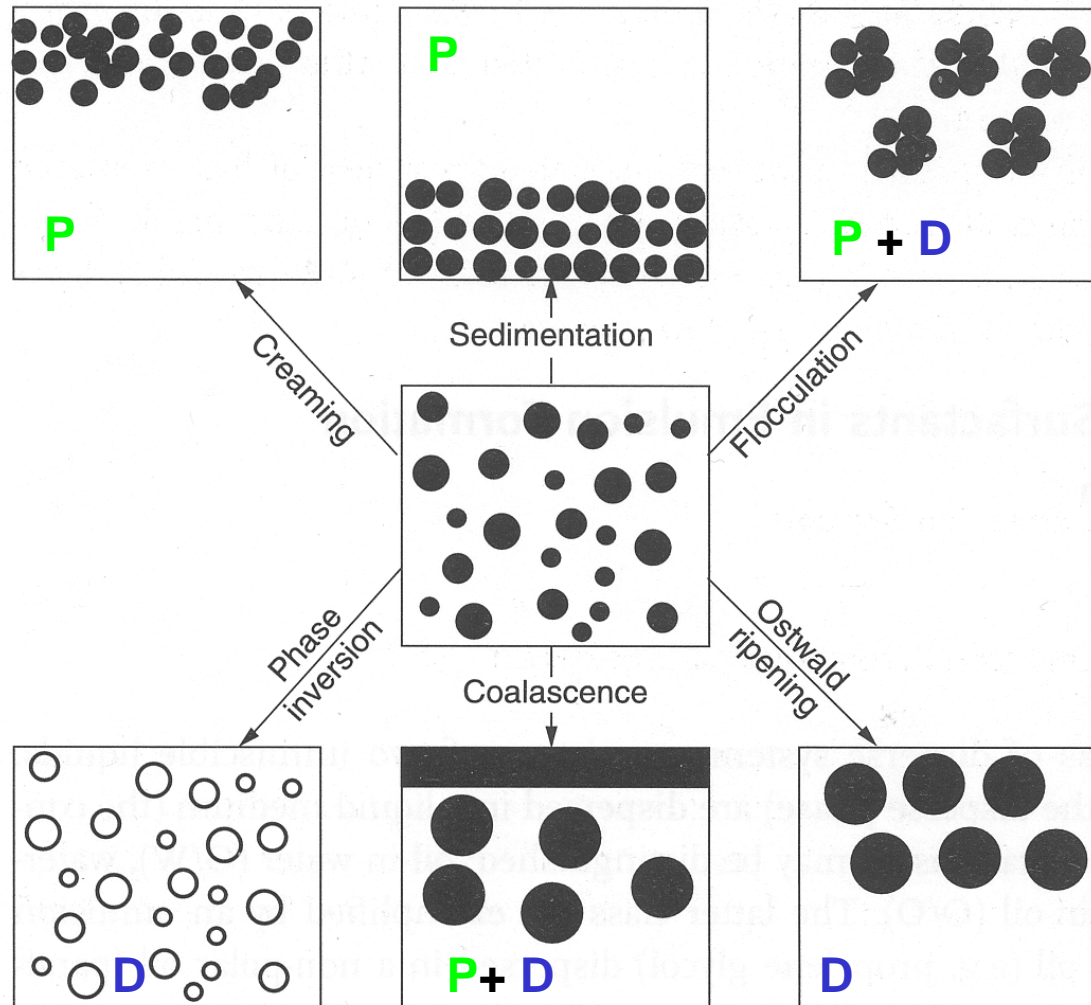
To define and to quantify the health is very complex.

It is easier to describe an illness, although descriptions are often also fuzzy.

1. Summary
2. Introduction
3. Terminology
4. Basics of stability
 - 4.1. Dispersions
 - 4.2. Characteristic features with regard to dispersion stability
 - 4.3. Alterations of the state of a dispersion
5. General aspects to characterize the change of the state of a dispersion
 - 5.1. Test-bottle testing by naked eye observation
 - 5.2. Analytical methods to characterize directly the time behaviour of the state of a dispersion
 - 5.3. Indirect analytical methods to measure a physical quantity related to the state of a dispersion
 - 5.4. Procedures to accelerate long-term stability

1. volume concentration of particulate phase
(diluted, semi-diluted, concentrated; homogeneity)
2. state of the continuous phase
(density, solvency, pH, ionic composition, rheological behaviour)
3. state of the particular phase
(size distribution, density distribution, morphology and shape, softness, surface structure)
4. interaction between particles
(repulsion, attraction, hydrodynamic)
5. interaction between particulate and continuous phase
(dissolution and deposition of particulate material, adsorption, electrostatic and electro-steric surface structure, structuring of the continuous phase)

Force driven and diffusion driven changes



P – Physical forces (gravity, centrifug., electrical fields, etc.) **D** – Diffusion driven

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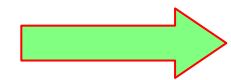
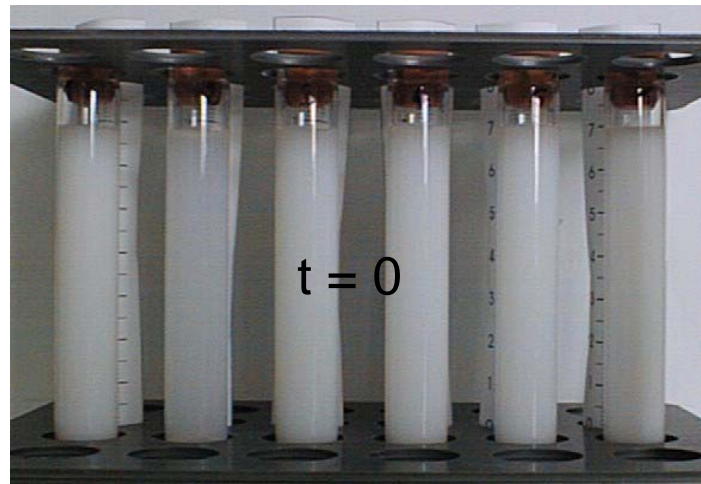
Stability may be either monitored (determined) in real time or predicted on the basis of physical quantities related to it.

.....

Guidelines will be given for choosing relevant measurements that can be used for the ranking, identification and quantification

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- ① **Direct** observation of the state by naked eyes (test-tube test, test-bottle test)



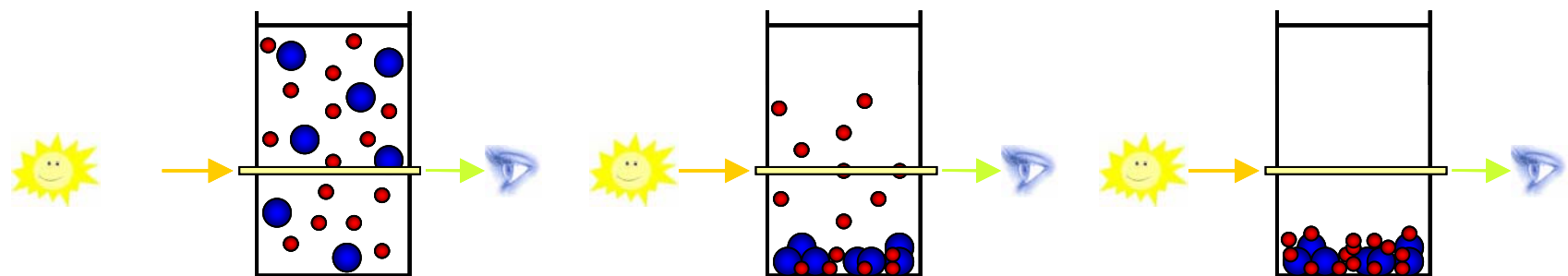
**Qualitative „yes/no“ or „more/less“
Simple and low cost**

Subjective, not traceable, time demanding

② Analytical methods to characterize directly the time behaviour of the state of a dispersion

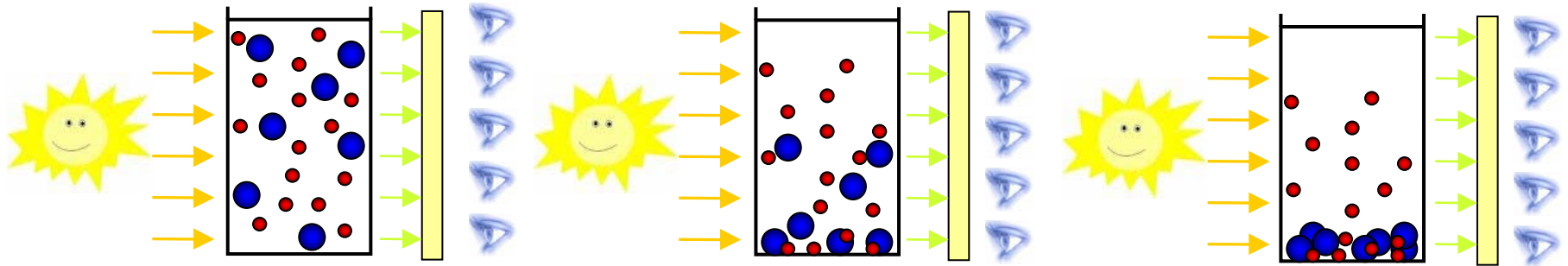
- A. Building up particle concentration gradients
- B. Alterations regarding size, agglomeration, coalescence, flocculation, etc. leading to non-homogeneities
 - 1. Microscopic examination of samples
 - 2. Optical methods
 - 3. X-ray methods
 - 4. Tomography
 - 5. Acoustic methods
 - 6. Conductivity methods

At a selected position

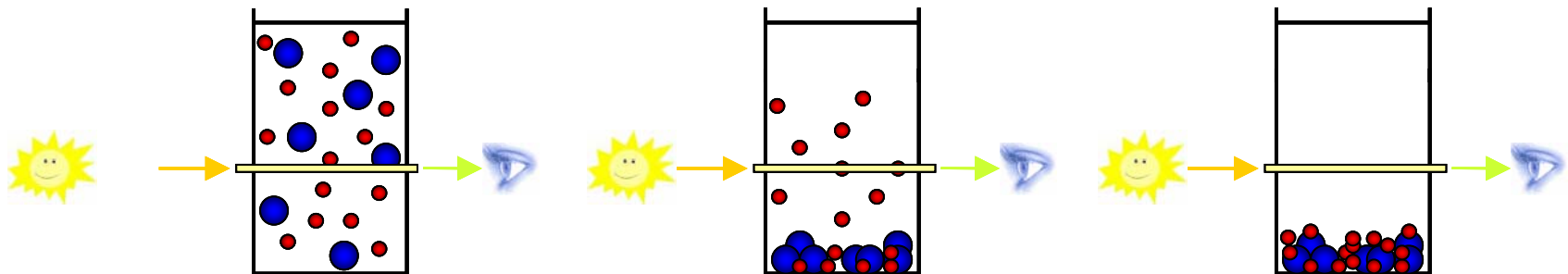


Space and Time resolved Extinction Profiles

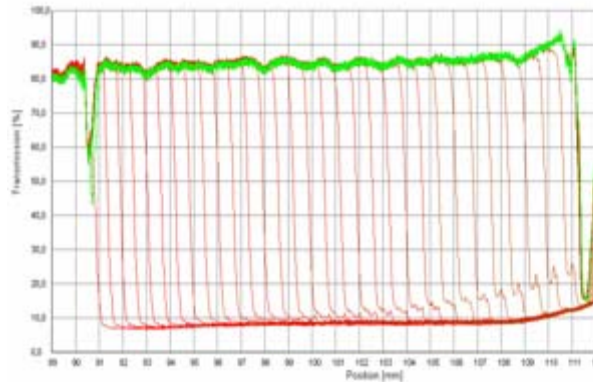
Any position at a selected time



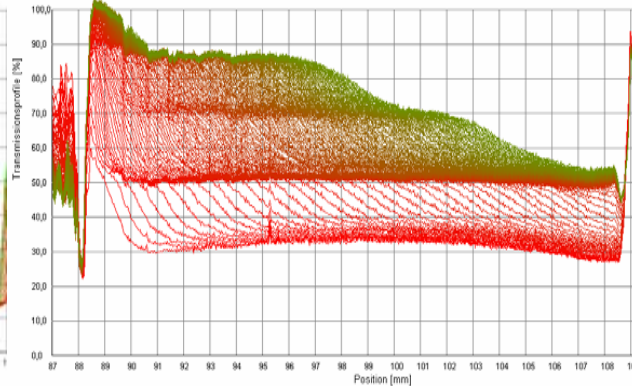
At a selected position and any time at a selected position



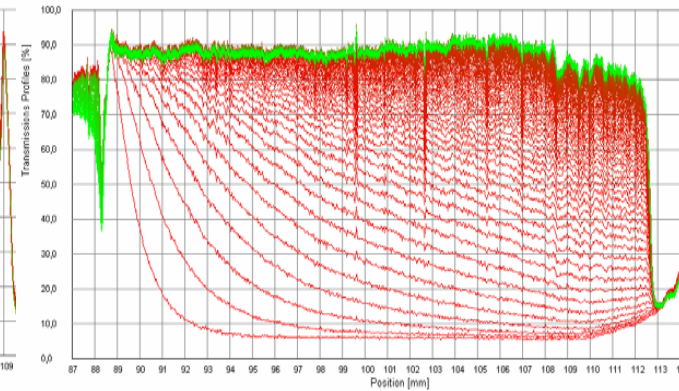
Suspension
monomodal monodisperse



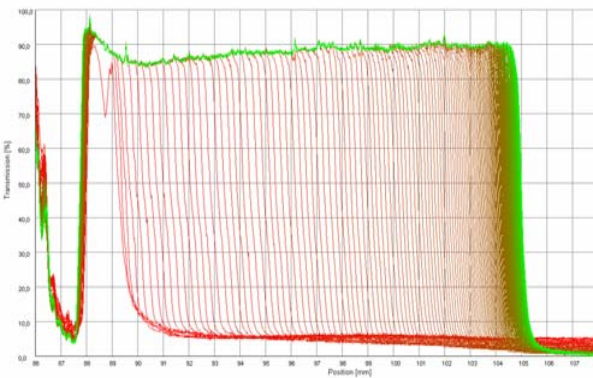
Suspension
tetramodal monodisperse



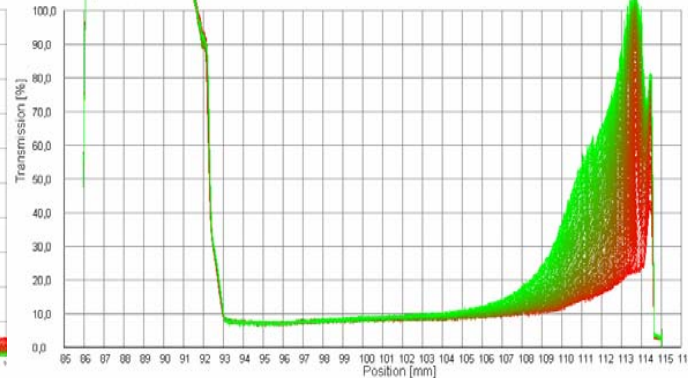
Suspension
polydisperse



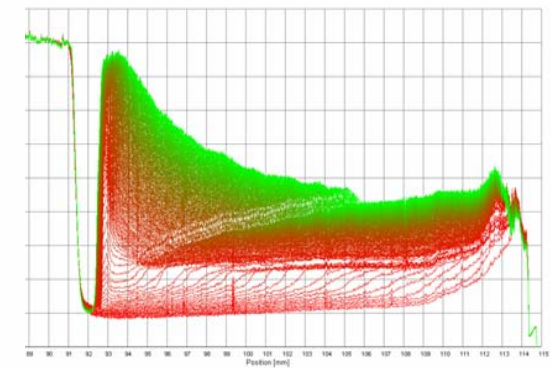
Suspension
particle – particle - interaction



Emulsion
rather monodisperse



Suspension
flotation and sedimentation

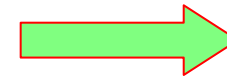


② Analytical methods to characterize directly the time behaviour of the state of a dispersion

A. Building up particle concentration gradients

B. Alterations regarding size, agglomeration, coalescence, flocculation, etc. leading to non-homogeneities

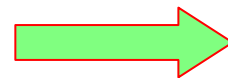
1. Microscopic examination of samples (SR > few mm)
2. Optical methods (SR=7 μm , 14 μm , 40 μm)
3. X-ray methods (SR about 30 μm)
4. Tomography
5. Acoustic methods (SR > 100 μm)
6. Conductivity methods (SR a few mm)



Quantitative data
Objective, traceable
Higher costs
(Should have space resolution)
Time consuming until

③ Indirect analytical methods to measure a physical quantity related to the state of a dispersion

1. Density differences
2. Mean particle size and size distribution
3. Shape
4. Electrophoretic mobility, Zeta-Potential
5. Concentration of particles/droplets larger than a stated size value.
6. Rheological parameters



Quantitative data

Objective, traceable

Higher costs

No waiting time

Calculation of a stability number or shelf life not possible

Scope:

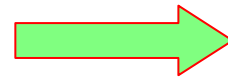
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The stability of a dispersion is defined in terms of the change in one or more physical or physico-chemical properties over a given time period. Stability may be either monitored (determined) in real time or predicted on the basis of physical quantities related to it.

In the case of very stable dispersions (nanoparticles), procedures that accelerate the changes under consideration or accelerating aging tests administered over a shorter time scale may be appropriate.

④ Procedures to accelerate the evaluation of long-term stability

0. Increase time and space resolution, new measuring principles
1. Inclination
2. Mechanical stress
 - a) centrifugation
 - b) shear forces, vibration, agitation
3. Thermal stress (storage at an appropriate climate, freeze-thaw cycles)
4. Chemical stress (salt, pH, solvent, additives (demulsifiers), etc.)
5. Combinations of the above procedures



Quantitative data

Objective, traceable

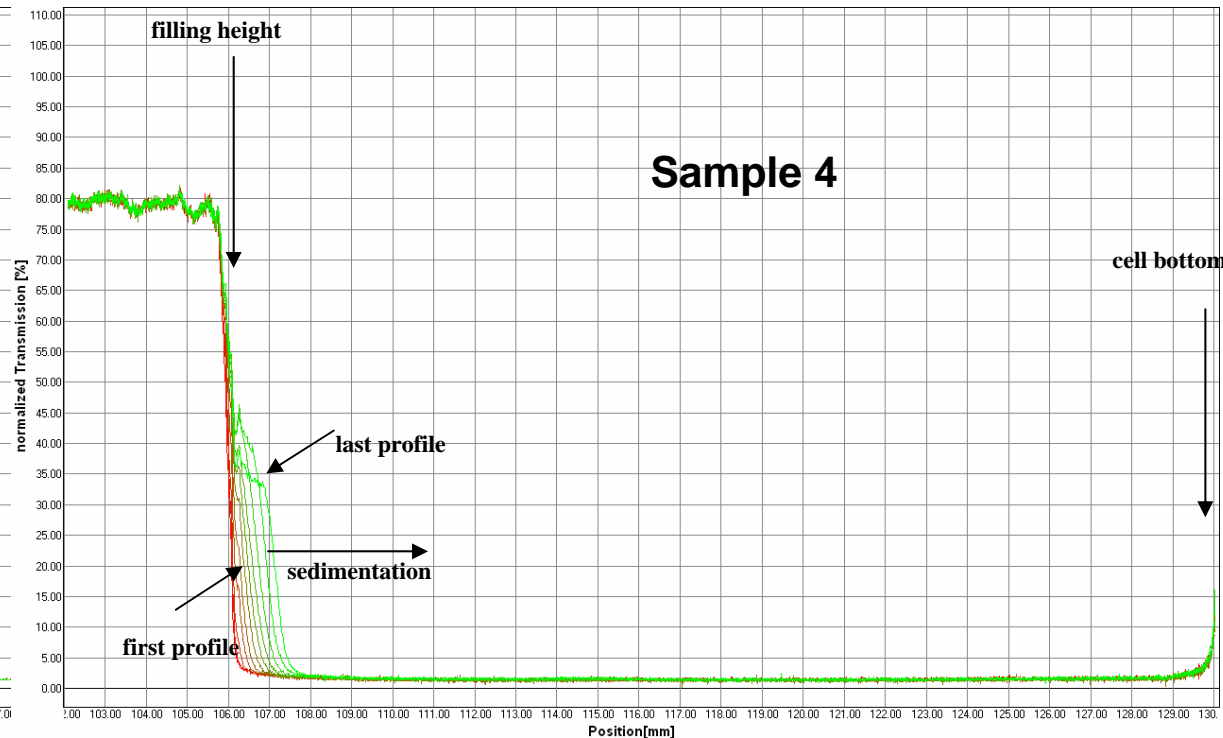
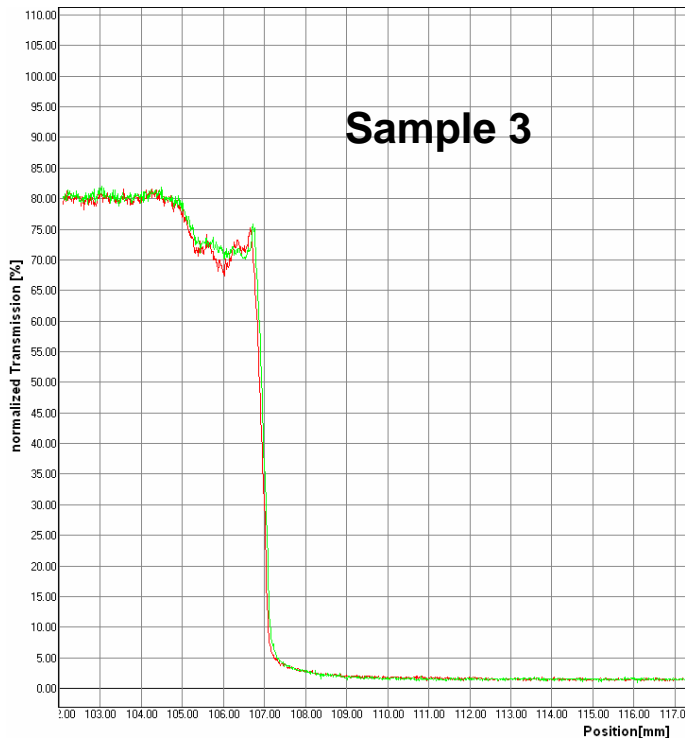
Reduced or no waiting time for natural destabilization

**Allows in general only sample ranking
Recalculation back to „normal
storage conditions“ not always given**

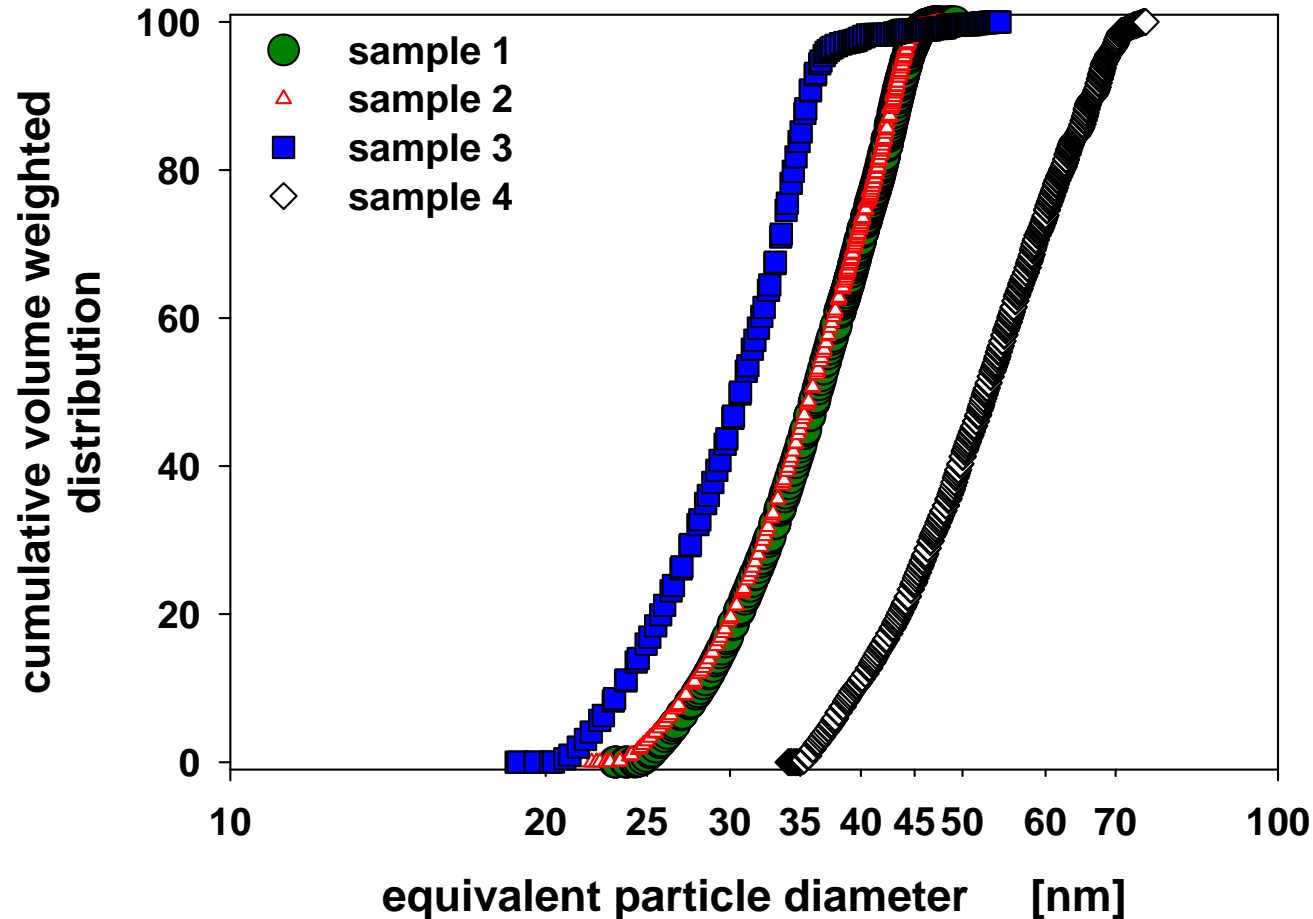
5.4.2. Acceleration by centrifugal forces

Stability evaluation (Finger prints) of Nanomaterial Carbon black samples (1 – 4)

2300 xg, 120 min, 20°C



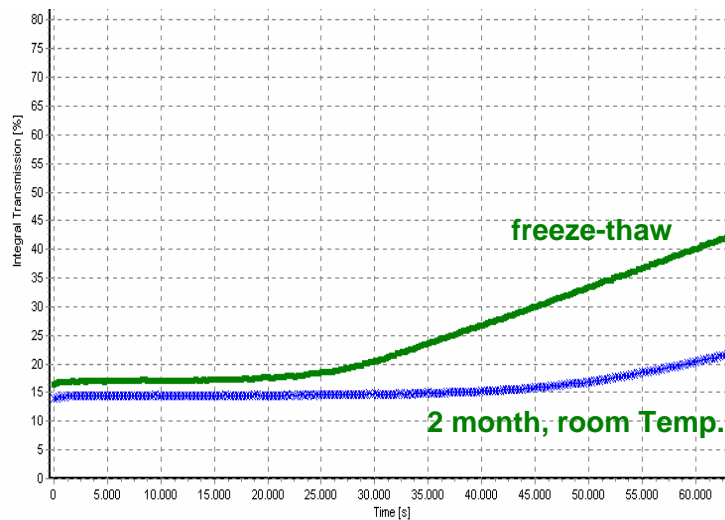
Ranking by Fingerprints/Integral Transmission $S3 < S2 \sim S1 < S4$ (less stable)



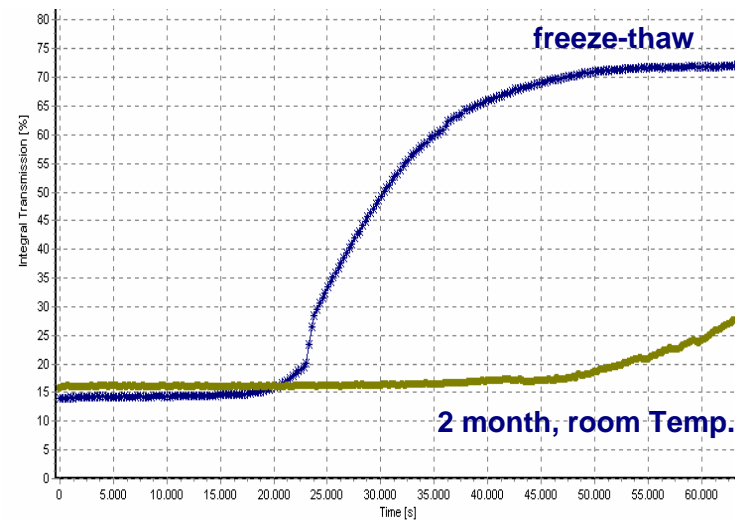
Ranking by Particle Size $S3 < S2 \sim S1 < S4$ (coarser)

„Normal“ aging and the effect of one freeze-thaw cycle

Cream A

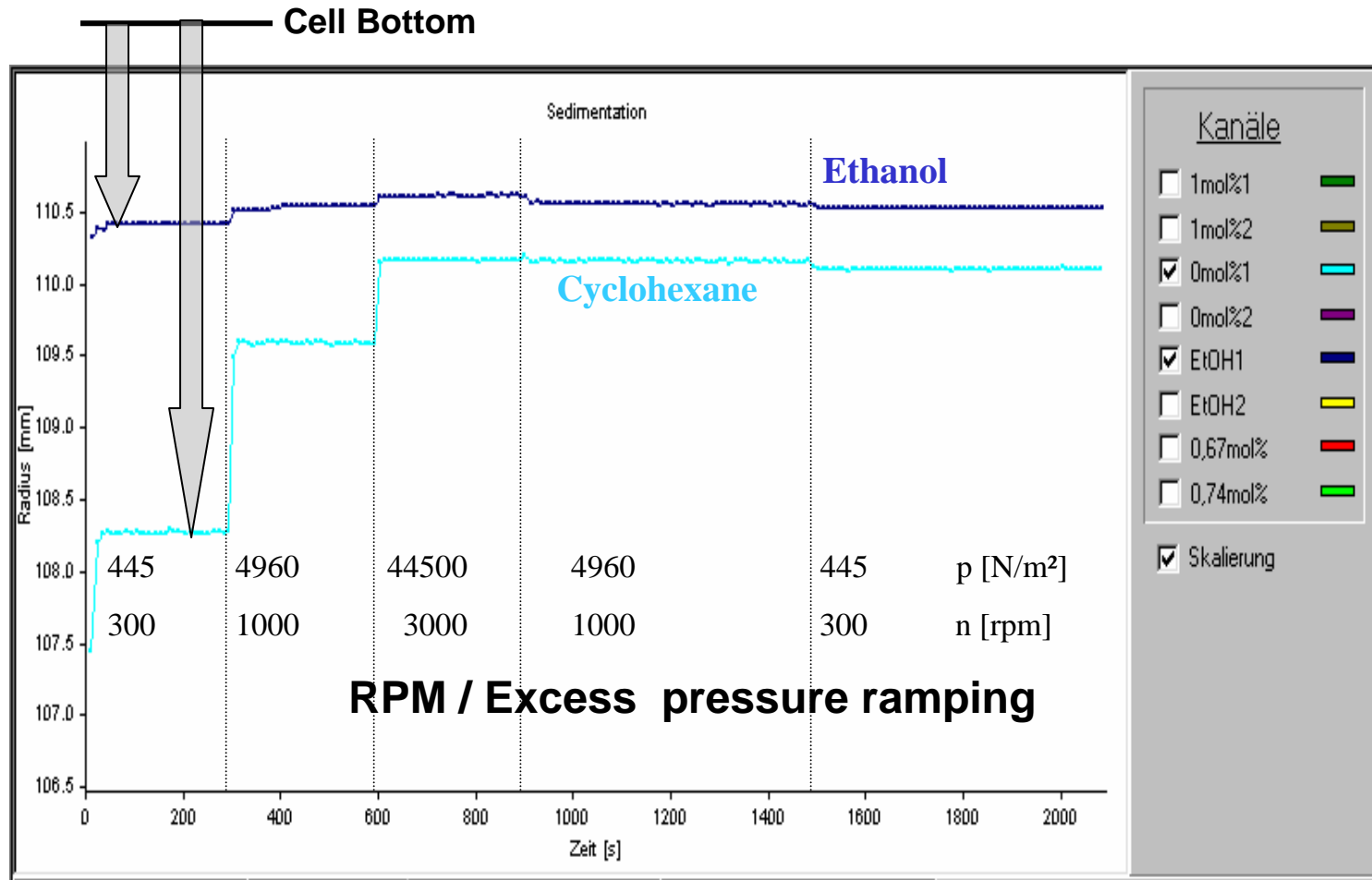


Cream B



Centrifugation: 18 hours at 3000 rpm corresponds to gravity phase separation of 3 years!!

5.4.4. Chemical stress (solvent)



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Shelf life may be estimated based on the observed rate of the change in the physical property and the user (customer)-demanded specifications for the product.

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 - 5.4. Procedures to accelerate long-term stability
 - 5.4.1. Inclination
 - 5.4.2. Mechanical stress
 - 5.4.3. Thermal stress
 - 5.4.4. Chemical stress
 - 5.4.5. Combinations
- 6. Prediction of the shelf life of a dispersion**
7. Conclusion
8. References
- Annex

Standard Procedure to Calculate Sedimentation Velocity at Gravity from LUMiFuge Data?

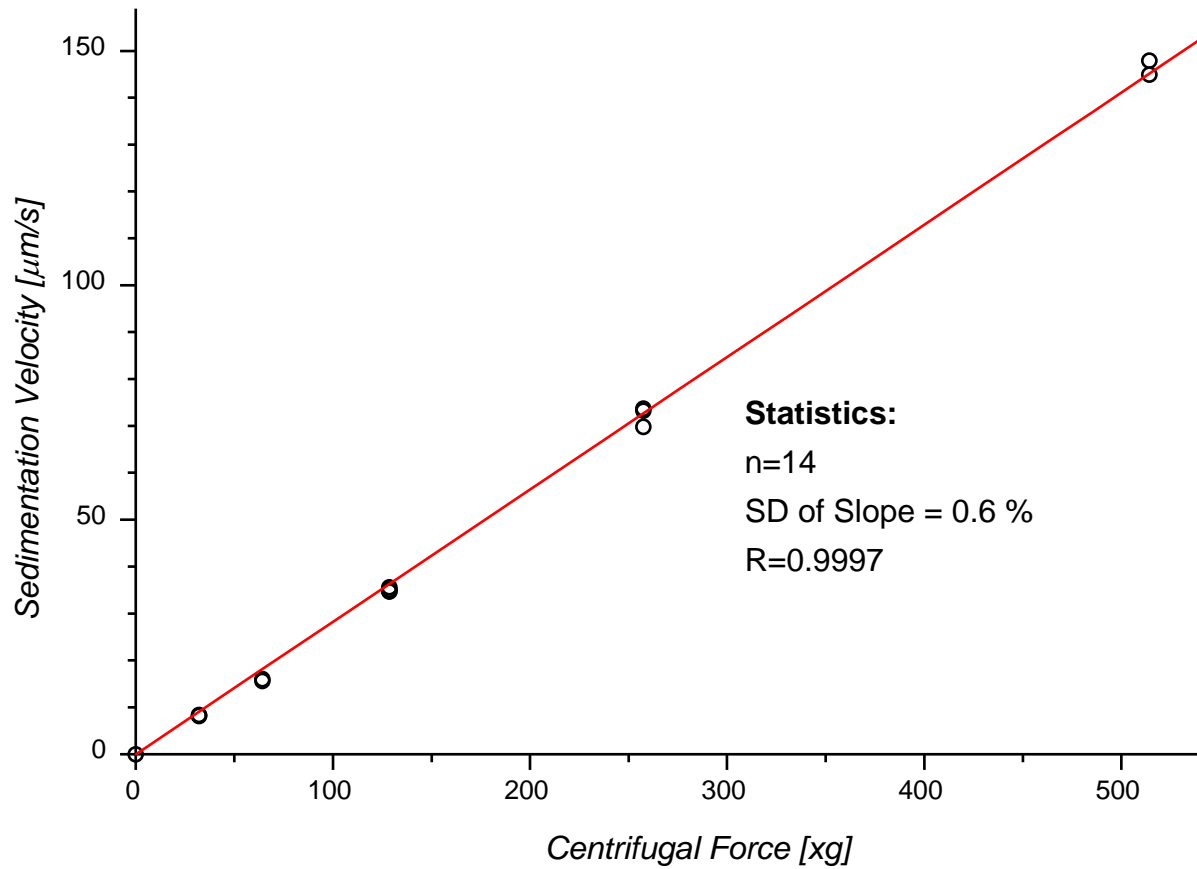
1. Convert rpm-settings into Relativ Centrifugal Force (RCF) (ratio centrifugal acceleration to that of gravity (1 xg))

$$\text{RCF} = \omega^2 \cdot R[\text{m}] / 9.81 = \text{RPM}^2 \cdot R[\text{m}] / (29.9093)^2$$

$$\rightarrow \text{RCF} = 1.1179\text{E-}3 * \text{RPM}^2 \cdot R[\text{m}]$$

2. Determine the dependency between the de-mixing velocity $V(\text{LF})$ and the RCF.

Sedimentation Velocities of a Latex Suspension at Different *RCF*

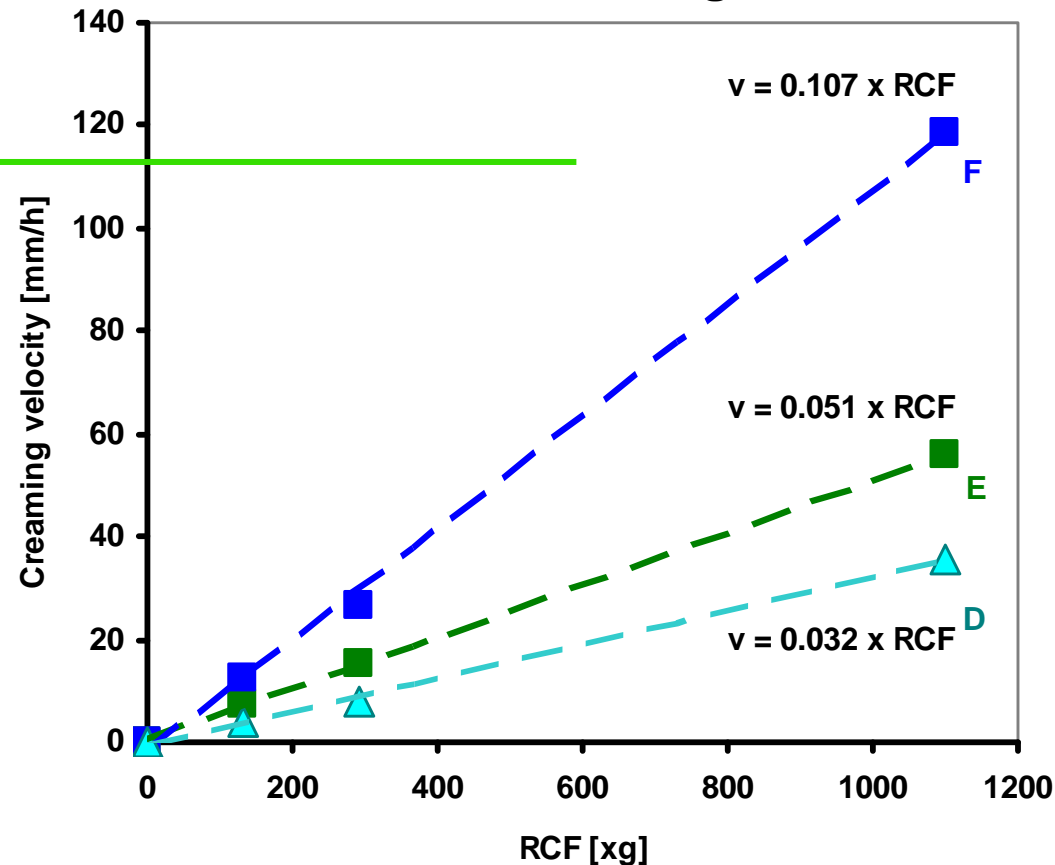


Important: Tell the statistical programm that the **line has to go through the origin !!!!!**

3. Calculation of shelf life

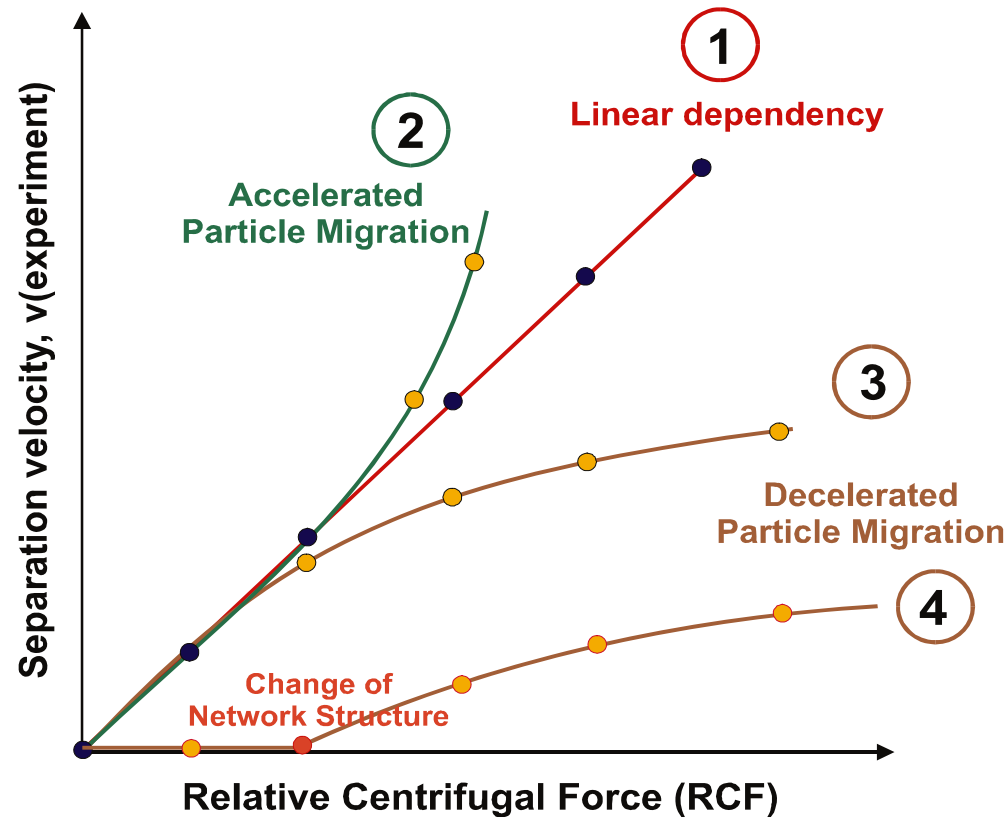


Alcoholic Milk Beverages



Stability Spec:
5 mm water layer at the bottle bottom

Sample	D	E	F
Calc. Shelf Life [days]	6.5	4.1	1.95



Force Resistant: ① Stokes' Law Applies
(70% of all applications)

Force Sensitive: ② ③ ④
i.e. shear induced aggregation,
Floc degradation, Break of gel structure

Conclusion:
Beside demixing stability also info
about shear force related behaviour

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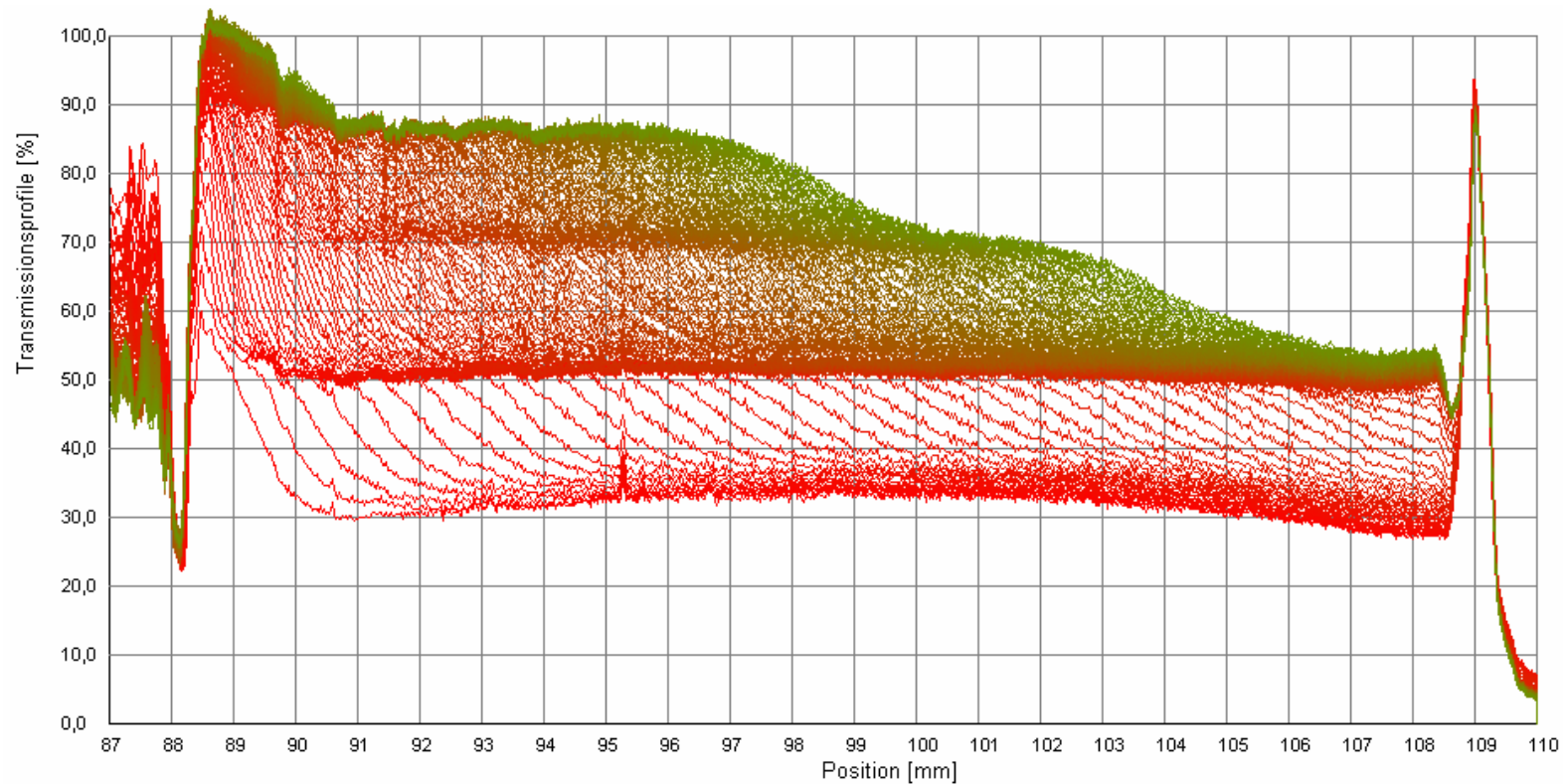
Annex

- A. Compilation of relevant international and national standards

1. ASTM D3342-90(2006) gives a method for measuring dispersion stability of oil/water dispersions by looking for phase separation.
2. ASTM D2205-85(2004) covers the selection and use of procedures for testing traffic paints.
3. Chinese standards GB/T 4468-1984 and GB/T 4467-2006 give methods for measuring dispersion stability in dye dispersions.
4. ISO 8780 parts 1-6 (1990) describe sample preparation for assessment of dispersion characteristics in pigments and extenders. The methods use various types of mechanical dispersion.
5. ISO 8781 parts 1-3 (1990) provide methods for assessing dispersion characteristics of pigments and extenders. Methods are based on the change in tinting strength of coloured pigments, change in the fineness of grind (Hegman gauge), and change in gloss.
6. DIN 53238-24 uses microscopy to assess ease of dispersion in pigments.
7. DIN EN 13900 parts 1-5 (2003) assess dispersability of pigments in polymers via 2-roll mixing; a filterability (filter pressure value) test is described in part 5.
8. ISO 14887 Sample preparation. Dispersing procedures
9. ISO 14703: Fine ceramics – sample preparation for PSD

2. Introduction to stability
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Thank you for your attention!



More Information:
Poster Session now 17.40:

Hall 6; Booth 6-114
T04-414; T04-417; T06-436; T06-468,
T08-421;