MICROTRAC

Fast and Reliable Sedimentation studies

How to quantify sediment kinetics, packing & redispersing?

Context

During their lifetime, many industrial products undergo a sedimentation phenomenon that greatly affects their end-use properties such as paint coverage, sunscreen efficiency, and drug dosage. As a result, it is crucial to anticipate the physical stability of these products during the formulation process. By limiting the settling process of particles, the shelf-life of the product can be improved, and easy redispersion ensures a consistent sample before use. This note shows how studying sedimentation can provide a rapid evaluation of shelf-life, allowing formulation comparison and quantification. Furthermore, detailed calculations are presented to fully understand the mechanisms of sedimentation.

Definition: Sedimentation

Sedimentation is a phenomenon that consists of solid particles settling at the bottom of the container over time. It is mainly observed in suspensions.

A suspension consists of a solid particle dispersed in a liquid phase. These systems are thermodynamically unstable and will destabilize until complete phase separation. The primary cause of instability is the difference in density between the solid particles and the continuous phase, which results in a migration phenomenon known as sedimentation.

Figure 1. Sedimentation in opaque samples

The sedimentation process can be quantified by the settling velocity expressed by the Stokes law:

$$v = \frac{\Delta\rho_p \, g \, d^2}{18\eta}$$

- v : Particle settling velocity
- g : Acceleration of gravity
- d: particle diameter (assuming spherical)
- η: Kinematic viscosity of the fluid
- $\Delta\rho_p$: Difference between mass density of the particle and the fluid

The analysis of Stokes Law provides insight into how to limit sedimentation. This can be achieved by increasing the viscosity of the continuous phase, reducing density differences, or reducing the average particle size. Sedimentation can also be **reversible** and dependent on various factors such as particle-particle interactions, cohesion energy, and sediment packing. The energy required for redispersion can vary from manual shaking for vaccines or beverages to mechanical stirring for paints or building materials. Therefore, redispersion efficiency should also be considered when studying sedimentation.

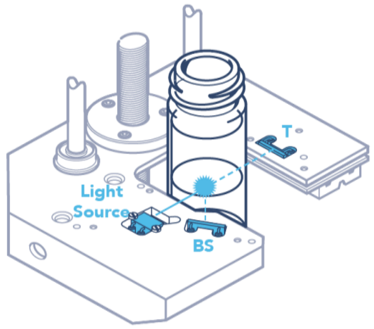
Sedimentation: Conventional test

Easy to implement, visual observation remains the most used method for sedimentation testing, and thus stability analysis. The method is simple but can be time-consuming as the variation must be visible to the naked eye to be detected. Additionally, the evaluation of the sedimentation kinetics is imprecise.

To overcome sedimentation issues, scientists need **early identification** and **quantification** to apply the best strategy and measure the benefit of stabilizing agent addition.

TURBISCAN: How it works

TURBISCAN technology, based on Static Multiple Light Scattering (SMLS), consists of sending light pulses (880 nm) into a sample along its height. The reading head scans the sample by moving vertically along the analysis cell and acquires data each 20 µm. Measurements are made over time and variations in the backscattering and transmission levels due to sample instability are recorded. The signal is directly linked to the evolution of particle concentration (φ) and size (d) by the Mie theory.



$$BS = f\ (\varphi, d, np, nf)$$

Figure 2. TURBISCAN measurement head

Samples with a particle concentration from **10^{-4} to 95% (v/v)** and from **10nm to 1mm** in particle size can be measured as is.

The instrument enables monitoring of changes in physical stability (coalescence, creaming, sedimentation, phase separation, etc...) **without any dilution or any stress** and thus follows **ISO TR13097 guidelines**.

ISO TR13097 defines scanning and spatially resolving techniques as perfectly suitable for stability analysis and suggests that the acceleration procedures applied to shorten test duration must not denature the initial product.

Sedimentation with the TURBISCAN

The recorded variations are represented as a function of sample height (in mm) over time. The bottom of the sample is represented on the left part of the graphic and the top of the sample is on the right part. The color gradient on the time scale corresponds to each scan time lapse with the first scan in blue and the last scan in red. The recorded backscattering level is put in "Delta Mode"- ΔBS.

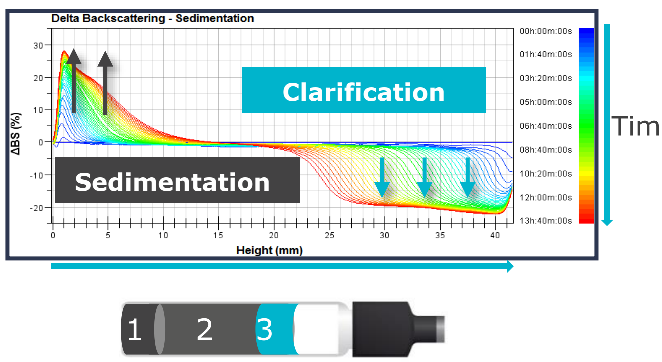


Figure 3. Sedimentation graph with TURBISCAN

The first scan is used as a reference to follow sedimentation evolution from the sample's initial state.

The above profile is an example of a sample analyzed for 14 hours with the TURBISCAN. The graph allows us to identify 3 key areas for data treatment:

- At the bottom of the sample (1) - left side of the graph- the Backscattering signal increases with time, which means more and more scatterers are present in this area. The particles sediment and locally change the suspension's concentration. A **SEDIMENT** is formed over time.
- At the top of the sample (3) - right side of the graph -, the Backscattering signal decreases, fewer scatterers are present at the top and the suspension becomes less concentrated. A **CLARIFICATION** layer is formed over time.
- In the central area (2), the Backscattering signal remains within the same level during the test, this indicates that the destabilization phenomenon is purely migratory, and no size variation is seen in this case.

Even in concentrated media, particle migration is identified within the **first hours** while it can take days and weeks to be visible by the naked eye. To evaluate stability.

Compare and select the best one

The TURBISCAN Stability Index (TSI) is an automatic calculation that sums all destabilizations into a single number for easy, one-click ranking and comparison. Therefore, **the HIGHER the TSI value, the LOWER the Stability** (for more information on the TSI, download the application note TS-Stab_60-TSI calculations).

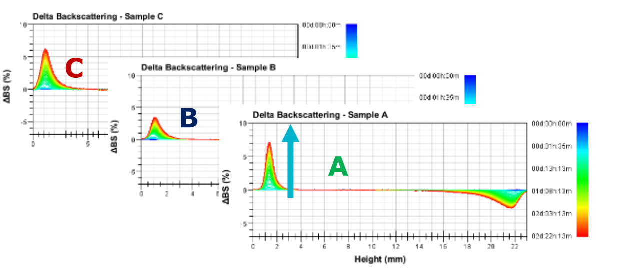


Figure 4. Sedimentation graphs for the 3 samples

Three suspensions (A, B, C) were studied with the TURBISCAN. The suspensions are simply poured into the 20mL glass vials and measured for 3 days at 25°C. In a single click, the TSI can obtained in function of time.

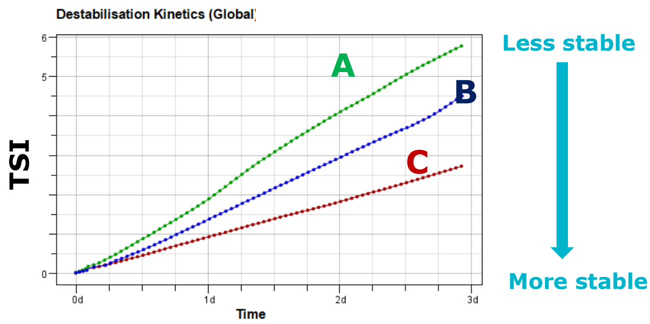


Figure 5. TSI kinetics over 3 days

The destabilization kinetic of sample C is slower than for sample B and A therefore sample C can be ranked as the **MOST STABLE**. Measurements were performed for 2 days, but sample classification is already possible within the first hours (8 hours).

What are the benefits of using the TURBISCAN?

Determining the best formulation requires many trials and strategies to limit or stop the sedimentation. To take a step back and accelerate the decision process, the stability testing must give precise and reliable answers (Go - No Go)

In addition to the fast detection (up to 200X faster), the sedimentation kinetics can be plotted with a single click calculation for an overall understanding and comparison. More detailed calculations are also available to provide a **deeper understanding** of the migration process to study the intensity, thickness of the layers, settling velocities details, and particle size.

Detailed understanding of the Sedimentation

As sedimentation progresses over time, the clarification front moves forward, and the sediment thickness and intensity increase in the bottom of the vial:

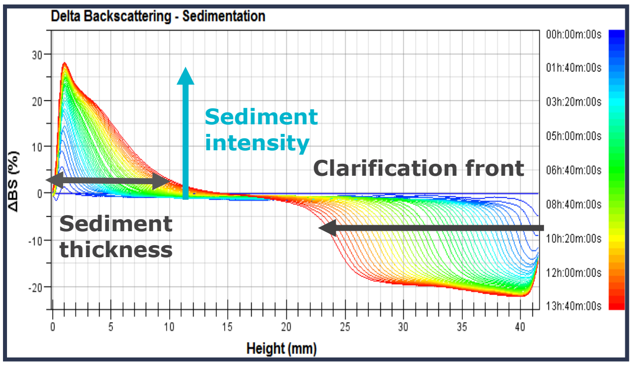


Figure 6. Sedimentation graph with all the phenomena

All these parameters can be monitored to understand the sedimentation process.

- *How significant is the sedimentation?*

As an example, the progression of the sedimentations for 3 samples A, B, and C is shown below: the mean values of Backscattered signal - ΔBS (left) represent the **intensity of sedimentation** and the peak thickness the sediment thickness (right):

Sample A is the sample with the highest concentration change (sedimentation intensity), and it generates the thickest sediment layer of 2.2mm after 3 days. The sediment thickness for samples B and C is similar after 3 days but sample C has a lower density sedimentation (lower concentration variation).

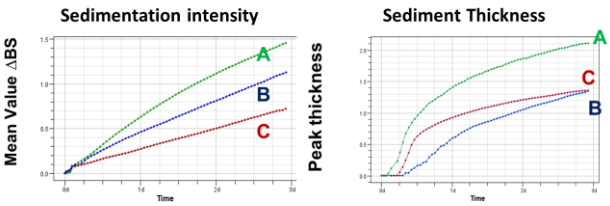


Figure 7. Sedimentation intensities and heights

- *How to calculate the exact settling rate and particle size of settling particles?*

The evolution of the clarification front enables to follow the settling rate of migrating particles.

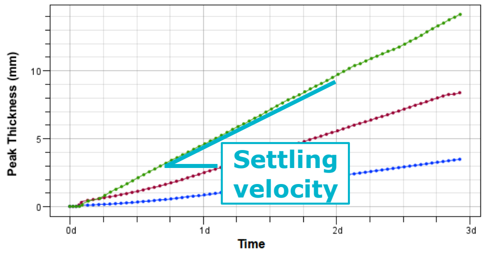


Figure 8. Settling velocities

Sample A presents the larger clarification front compared to B and C. The slope of each curve corresponds to the speed of migration of the clarification front. In other words, to particle settling rate. Particles of sample A are settling faster than samples B and C.

Based on the Stokes equation, adapted to concentrated media, the settling particle diameter or so-called hydrodynamic diameter can be evaluated by adding the necessary information.

Sample	Settling velocity	Hydrodynamic
Sample A	0.211 mm/hour	0.38 µm
Sample B	0.056 mm/hour	0.20 µm
Sample C	0.128 mm/hour	0.25 µm

Table 1. Settling velocities and sample particle size

This diameter corresponds to the diameter of the particle in motion. If the clarification front kinetic is not linear (multiple slopes) hence the particle size of each population can be determined to give the particle size distribution.

How easy it is to redisperse the suspension?

TURBISCAN enables to follow the re-dispersion process under agitation, directly in the measurement vial. The evolution of the backscattering value over time as the particles are re-suspending can be monitored and a recovery rate can be calculated (measured BS / initial BS value). Based on this method, we can easily study the ease of redispersion and the optimum time to recover most of the initial state.

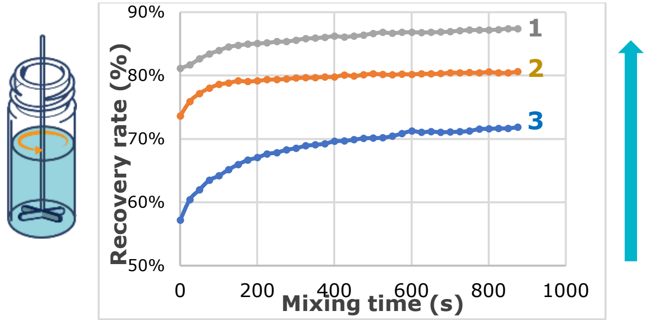


Figure 9. Recovery rates over mixing time

Samples 2 and 3 show a lower recovery rate (<80%) while Sample 1 shows the best redispersion properties with the highest recovery rate - up to 87%. Sample 1 will provide the easiest product to redisperse and thus extend product shelf life.

Conclusion

TURBISCAN technology based on Static Multiple Light Scattering (SMLS) enables to study of sedimentation in concentrated media **without any dilution or mechanical stress**. Sedimentation is detected faster compared to the eye **(200x faster)**. The TURBISCAN allows not only detection but also to **quantify** the sedimentation, either with the TURBISCAN Stability Index (TSI) or by plotting detailed kinetics. Based on these reliable results, the choice of the strategy to apply to overcome sedimentation is made more objectively.