

STABILITY OF VARIOUS BEVERAGE EMULSIONS

Abstract

Beverage emulsions are very common on the market as they comprise all dairy based drinks and many of the soft drinks, which are diluted emulsions. All of these products show typical colloidal instabilities (creaming, sedimentation, flocculation, coalescence). Therefore, it is important to test their stability in the less possible time in order to improve the delivery period from the development to the production and, by doing so, follow the expectations of the consumers in the most efficient way. All these destabilizations can be monitored and quantified using the Turbiscan LAB or Classic. Analyses are done on the real product, without dilution and can be accelerated through temperature increase and automated with the ageing station (Turbiscan ags).

Keywords: milk, soft drink, emulsion, stability, Turbiscan®.

Introduction

The food industry develops more and more beverage based on emulsions. These can be originated from milk, with many different variations depending on the application required: different flavours from the old chocolate milk to the new fashionable mixtures of milk and juice; different additives giving milk enriched in vitamins, calcium, minerals for healthy drinks; *etc.* However, addition of these different raw materials into an already metastable colloidal product, which is milk, leads to important instabilities needed to be solved by the formulator.

On the other hand, many soft drinks are made from concentrated emulsions, which are diluted in aqueous solutions in order to simplify the production and reduce the supply chain cost as much as possible. However, here again colloidal instabilities arise and need to be controlled in order to ensure good quality products.

In addition to these physico-chemical problems, the formulator has to develop more and more new products in order to satisfy the consumers' requirements for new tastes. To be able to follow this challenge in a very competitive market, he needs to develop good quality drinks in the shortest possible time.

In this paper, we propose a unique tool, the Turbiscan®, to help the formulator in his day-to-day job of identifying and monitoring instabilities. Various behaviours of beverage emulsions are described as they are shown with the Turbiscan®.

Experimental procedure

1. Principle of the measurement

The heart of the optical scanning analyser, Turbiscan®, is a detection head, which moves up

and down, along a flat-bottom cylindrical glass cell (Figure 1)^{1,2}. The detection head is composed of a pulsed near infrared light source ($\lambda = 880 \text{ nm}$) and two synchronous detectors. The transmission detector (at 180°) receives the light, which goes through the sample, while the backscattering detector (at 45°) receives the light scattered backward by the sample. The detection head scans the entire height of the sample, acquiring transmission and backscattering data every $40 \mu\text{m}$. The Turbiscan LAB can be thermo-regulated from 4 to 60°C and linked to a fully automated ageing station (Turbiscan ags) for long-term stability analyses. Increasing temperature is the ideal parameter to accelerate destabilisation processes, while maintaining realistic testing conditions.

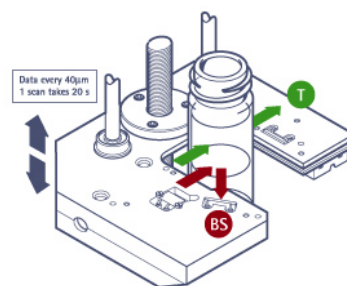


Figure 1. Principle of Turbiscan® measurement

The Turbiscan® makes scans at various pre-programmed times and overlays the profiles on one graph in order to show the destabilisation. Graphs are usually displayed in reference mode, whereby the first profile is subtracted to all other profiles, in order to enhance variations. A stable product has all the profiles overlaid on one curve (Figure 2), as an unstable formulation shows variations of the profiles (Figure 3). Backscattering and/or

transmission fluxes are shown in ordinate and the height of the cell in abscissa (Figure 2 and 3). The first profile is displayed in pink, the last one in red.

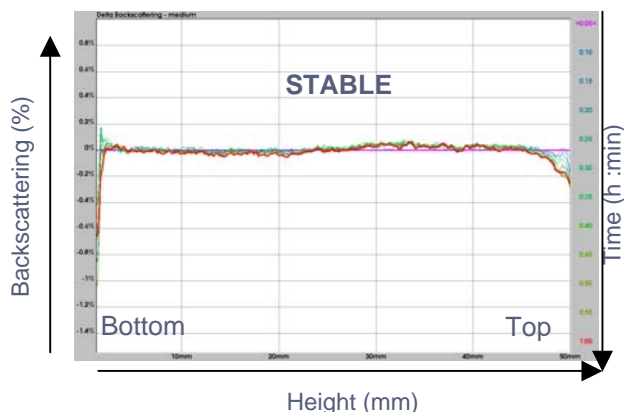


Figure 2. Superposition of scans with time for a stable sample

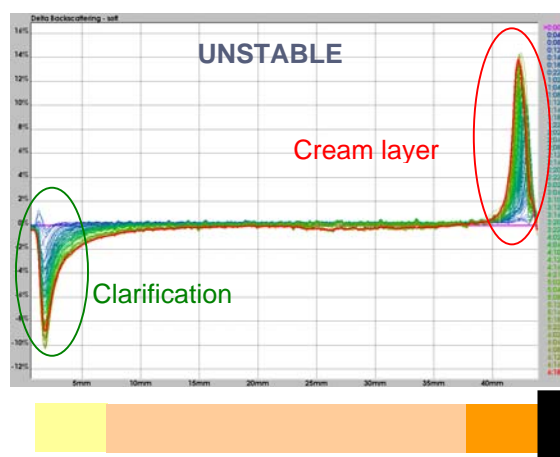


Figure 3. Superposition of scans with time for an unstable sample (creaming)

2. Instability detection

The measurement principle of the Turbiscan® range is based on multiple light scattering (MLS), where the photons are scattered many times by the particles / droplets of the dispersions before being detected by the backscattering detector. The intensity of the light backscattered by the sample depends on three parameters: the diameter of the particles, their volume fraction and the relative refractive index between the dispersed and continuous phases. Therefore, any change due to a variation of the particle size (flocculation, coalescence) or a local variation of the volume fraction (migration phenomena: creaming, sedimentation) is detected by the optical device.

a. Particle size variation

Figure 4, the variation of the backscattering level is shown as a function of the particle diameter for a fixed volume fraction of latex particles.

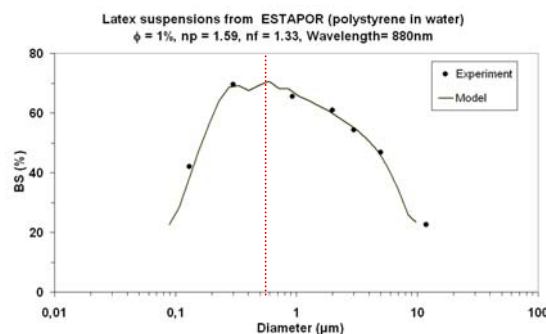


Figure 4. Backscattering level versus diameter for latex particles at 1%

The curve obtained is a bell shaped curve, where the top is linked to the wavelength of the incident light (880 nm). For particles smaller than the incident light (left part of the curve), an increase of particle size is showed by an increase in backscattering. For particles bigger than the incident light (right part of the curve), an increase in size leads to a decrease in backscattering.

On the Turbiscan® profiles, the particle size variations are displayed by a variation of the backscattering level over the total height of the sample (Figure 5).

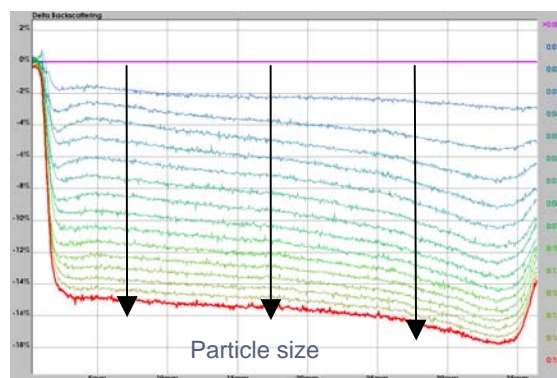


Figure 5. Typical profiles for flocculation phenomenon (initial size = 1µm)

b. Migration phenomena

Migration phenomena (sedimentation or creaming) lead to local variation of the concentration of particles in the sample.

Figure 6, the variation of transmission and backscattering levels are shown as a function of the volume fraction for a fixed diameter of latex particles.

If the concentration of particles is smaller than the critical concentration ϕ_c , the product can be considered as diluted and the transmission level decreases with an increase in concentration.

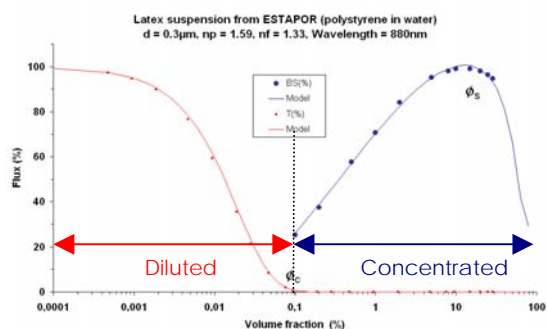


Figure 6. Transmission (red) and backscattering (blue) levels versus volume fraction for latex particles of $0.3 \mu\text{m}$

When the concentration is sufficient ($\phi > \phi_c$), there is no transmission signal (opaque product) and the backscattering level increases with an increase of the volume fraction.

When the concentration of particles becomes too high ($\phi > \phi_s$), the backscattering level starts to decrease as the distance between particles is smaller than the wavelength of incident light. This phenomenon is called dependent diffusion and is mostly observed for small particles ($< 1 \mu\text{m}$).

On the Turbiscan® profiles migration phenomena are displayed by local variations of the backscattering. Figure 7, the backscattering level decreases at the top (right part of the graph), due to a decrease of the concentration of particles, hence a clarification, while it increases at the bottom due to the increase of particle concentration consecutive to the sediment formation. It is interesting to note that there is no variation in the middle of the sample, indicating no particle size variation.

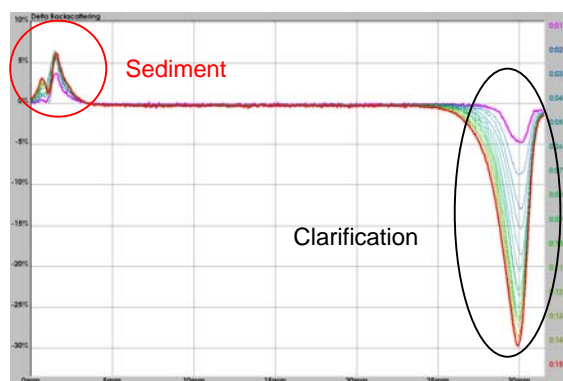


Figure 7. Typical backscattering profiles for a sedimentation phenomenon.

3. Materials

Various types of beverage emulsions based on milk or concentrated emulsions for soft drinks are described. The effect of temperature has also been investigated.

For each experiment, the sample was shaken before use and 7 or 20 mL (for the Turbiscan Classic and LAB respectively) was sampled in a borosilicate glass cell. The cell is then closed with a stopper and placed in the Turbiscan®.

Results and discussion

1. Colloidal stability of milk

Milk is a complex colloidal system comprising a mixture of fat globules, casein micelles and various minerals (e.g. calcium) in a water continuous phase. This system is stable for only a short period of time and many different parameters such as particle size^{3,4}, casein concentration, etc. influence the stability. One of the major instability phenomenon taking place in milk and milk based products is depletion flocculation^{5,6}.

Depletion flocculation occurs in milk due to the co-existence of casein micelles and fat globules. When two droplets come to such a distance that the casein micelles are driven out of the volume separating the fat globules, an osmotic pressure is created leading to an aggregation of the droplets. This aggregation has a direct influence on the creaming velocity⁵.

To illustrate this phenomenon, an analysis of half-skimmed milk has been done at 30°C during two days.

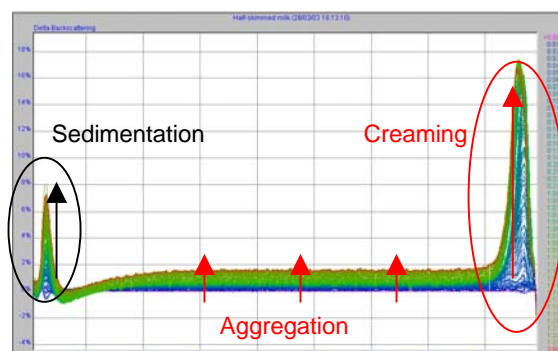


Figure 8. Backscattering profiles of half-skimmed milk (reference mode).

The profiles show an increase of the backscattering in the middle of the sample, which is characteristic of a particle size increase. Moreover, in the top part of the sample (right part of the graph), we can observe an important increase of the backscattering. This is due to an increase of the concentration of fat globules in this part. Creaming velocities can be computed from this experiment and samples easily compared.

2. Effect of flavour on milk-based drink

The formulation of drinks that are milk-based with addition of various fruit flavours is getting more and more fashionable in the European market and has been well known in Japan for many years. The addition of these kinds of flavours in dairy products is critical as it leads to an important decrease of the pH, hence a modification of the colloidal stability of the system.

A sample of fermented milk was studied with and without flavour at ambient temperature for 19 hours in the Turbiscan Classic. The typical behaviour is shown in Figure 9 in reference mode (first scan subtracted to all other scans) in order to facilitate the instability visualisation.

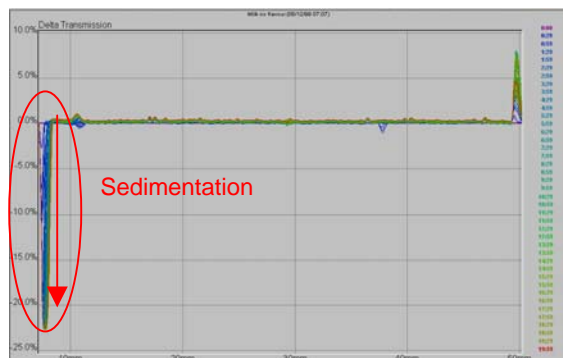


Figure 9. Transmission profiles of drink with no flavour (reference mode).

The signal obtained is in transmission as the system has a low concentration of dispersed phase. We observe a decrease of the signal at the bottom of the sample and an increase at the top, which is characteristic of a sedimentation phenomenon. As the milk is fermented, the system comprises small casein aggregates that are settling.

The addition of an acidic flavour (lemon) in the system leads to an acceleration of the aggregation of the caseins micelles, showed by the increase of the transmission level in the middle of the samples (Figure 10). This variation is small when no flavour is present (red curve) and increases when the flavour is added (orange curve).

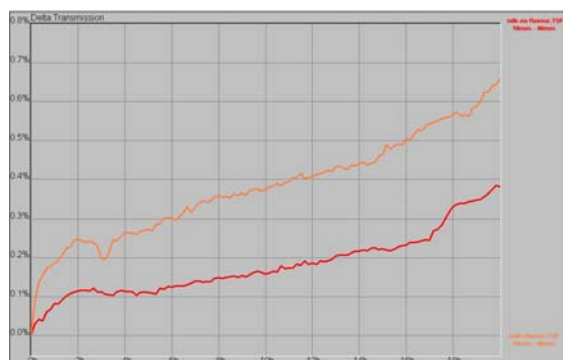


Figure 10. Aggregation of the casein micelles upon addition of acidic flavour.

When looking at the sedimentation taking place, it is possible to compute the sediment layer thickness (Figure 11).



Figure 11. Peak thickness of the sediment layer upon addition of acidic flavour.

This graph shows the effect of the flavour (orange curve) in the acceleration of the sedimentation of the particles in the drink. Therefore, the Turbiscan® enables to monitor the destabilisation of the colloidal properties of the system upon addition of flavours.

3. Effect of calcium addition in milk

Many dairy products now offer enriched-calcium compositions, in order to increase the calcium intake, as it has been discovered in the recent years that calcium not only helps for children growth, but also contributes to decrease various cardiovascular diseases and cancers for adults. However, this excess of calcium in milk can lead to serious instabilities, especially regarding protein stability. Therefore, some work has to be performed in order to obtain stable high concentration calcium milk products.

Different formulations of enriched-calcium milk have been tested over 50 days at ambient temperature in the Turbiscan Classic. The typical behaviour encountered is shown Figure 12.

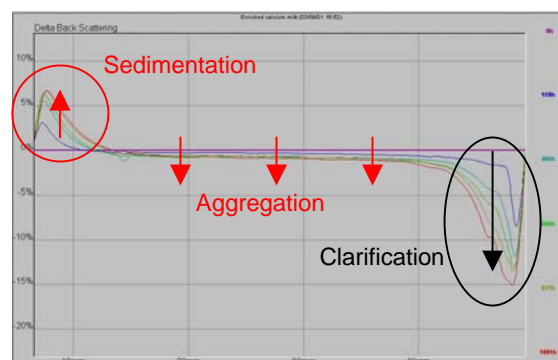


Figure 12. Backscattering profiles of enriched-calcium milk (reference mode).

The graph displays different instabilities. An increase of the backscattering level at the bottom (left part of the graph), characteristic of an increase of the concentration of dispersed phase in this part of the sample. This is coupled with a decrease of the backscattering level at the top, which is due to the clarification linked to the sedimentation taking place. This phenomenon can be followed by computing the thickness of the sediment peak at the bottom (Figure 13), which is a direct measurement of what would be measured by the eye, shall the sediment be visible. In this example, the sediment is 2.8mm large after 50 days of analysis.

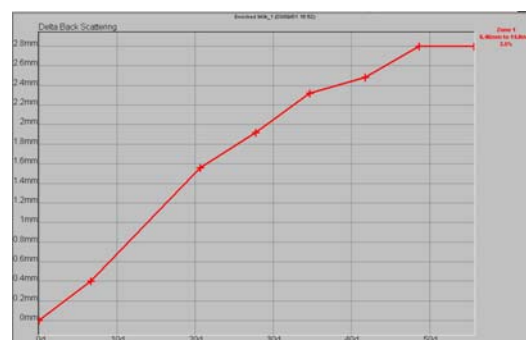


Figure 13. Peak thickness of the sediment layer.

Secondly, we can observe a slight decrease of the backscattering in the middle of the cell, due to a particle size increase (flocculation or coalescence). This effect is not surprising, as calcium is known as having a direct effect on the protein aggregation.

4. Stabiliser choice for chocolate milk

When formulating chocolate milk, any dairy drink for infant or complete nutritional formula, it is necessary to add stabilisers in order to overcome stability issues described in the previous examples. These compounds are usually biopolymers such as carrageenan, which act both as thickening and surface active agents.

It is therefore interesting to compare various stabilisers to select the best candidate for the optimal formulation. To do so, we present an experiment with three different stabilisers, used to stabilise a chocolate milk formulation. The samples were prepared through conventional method and their stability studied with the Turbiscan Classic at ambient temperature for 50 days. The typical behaviour observed is shown on Figure 14.

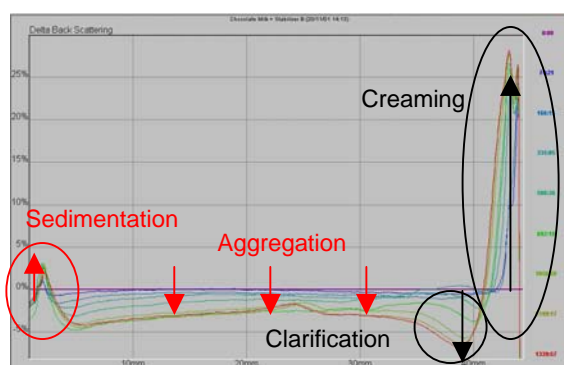


Figure 14. Backscattering profiles of chocolate milk (reference mode).

The profiles show all the different destabilisation phenomena taking place:

- A sedimentation phenomenon of the cocoa particles with increase of the backscattering level at the bottom and decrease at the top, as for the example presented previously.
- An aggregation of the cocoa particles showed by the decrease of the backscattering on the whole height of the sample.
- A creaming phenomenon shown by the increase of the backscattering at the top of the sample (right part of the graph).

All these phenomena take place simultaneously but can be identified and followed separately.

Firstly, we focus on the effect of the stabilisers on the sedimentation phenomenon through the migration velocity (Table 1). The calculation is integrated in the Turbisoft and is performed on the clarification layer.

Stabiliser	Migration velocity (10^{-5} mm/min)
1	16.6
2	8.2
3	3

Table 1. Migration velocities for various stabilisers

The results show that stabiliser 3 is the most efficient in preventing the migration of the cocoa particles.

Secondly, we look at the effect of the different stabilisers on the aggregation. To do so, we compute the variation of backscattering in the middle part of the samples (Figure 15).

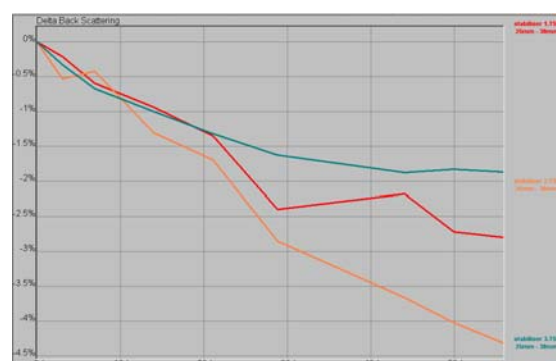


Figure 15. Effect of the stabilisers on aggregation.

From this graph, we can deduce that stabiliser 3 (green curve) is also the most efficient in preventing the aggregation of the cocoa particles.

To finish, we study the effect of the stabilisers on the creaming phenomenon. This is done by computing the phase thickness of the cream layer (Figure 16).

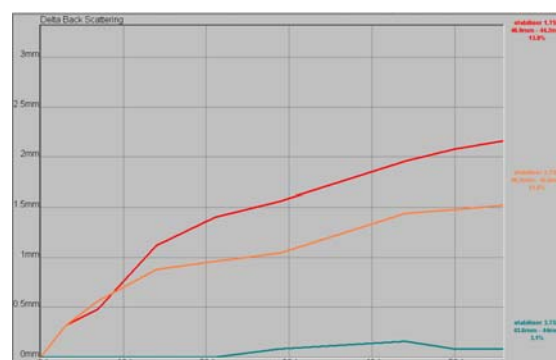


Figure 16. Effect of the stabilisers on creaming.

Here again stabiliser 3 (green curve) shows the largest impact on the creaming of the fat globules. The migration is almost completely inhibited.

Using the Turbiscan[®], we have shown that stabiliser 3 was the most efficient in getting a stable formulation. The comparison of the additives can be done easily through different parameters depending on the instability taking place.

5. Effect of the temperature on concentrated emulsions

Concentrated emulsions are widely used in the soft drink industry as a key intermediate of the production. They are made of an essential oil, which

bring the flavour to the drink, stabilised in a water base. They are then diluted in a sugar solution in order to obtain the final soft drink, which can then be carbonated for fizzy drinks. These emulsions need to be stable during the manufacturing process and have a direct impact on the stability of the final drink.

An interesting parameter to study is the effect of the temperature on the stability of the emulsion. This has been done by putting a concentrated emulsion sample at three different temperatures: 25, 35 and 45°C. These emulsions have been analysed for 24 hours in the Turbiscan®. They all show a creaming phenomenon and the migration velocities of the droplets are computed for each analysis (Table 2).

Temperature (°C)	Migration velocity (mm/h)
25	1.10
35	1.30
45	1.75

Table 2. Migration velocities for various temperatures

We can see on this table that after only 24 hours, it is possible to observe differences between the different temperatures, with an increase of the migration with increasing temperature. Therefore, it is interesting to increase the temperature of the analysis in order to accelerate the destabilisation and get results even sooner.

6. Study of ring formation in soft drink

The last example of application in the study of stability in beverage emulsions is the ring formation for soft drink. This is a parameter directly visible by the consumer and which can cause major rejection regarding the quality of the product. Its measurement is often left to the visual observation of the sample with all the subjectivity and the inaccuracy that it implies.

The example reported here concerns a finished soft drink (diluted emulsion) after decarbonation measured during 12 hours with the Turbiscan LAB at ambient temperature. As the product is diluted the equipment measures transmission (Figure 17) except where a ring forms at the top of the beverage due to creaming when backscattering is measured (Figure 18).

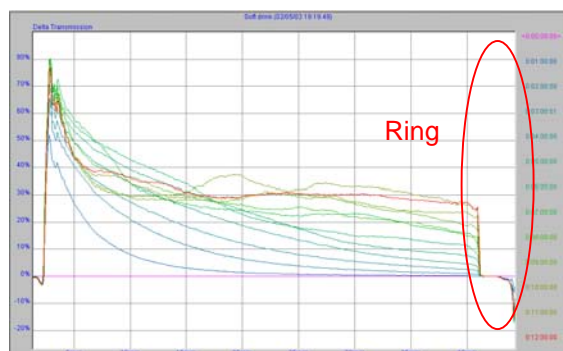


Figure 17. Transmission profiles of a soft drink (in reference mode).

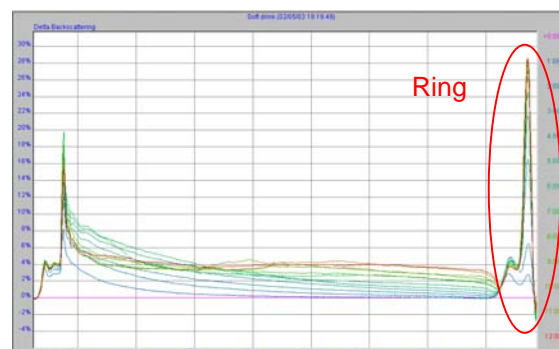


Figure 18. Backscattering profiles of a soft drink (in reference mode).

Figure 18, an increase of the backscattering is observed at the top of the sample (right part of the graph). It is due to an increase of the concentration of oil droplets in this part of the graph, hence a creaming phenomenon. The ring formation is therefore easily detected. By monitoring the variation of the backscattering at the top of the sample, it is possible to compare samples very easily. This parameter can be used for quality control after drink manufacturing.

One of the ways to avoid ring formation is the use of weighting agent to match the density of the dispersed and continuous phases⁷. As an example, we present (Figure 19) the results obtained for a series of drinks with various densities of oil phase.

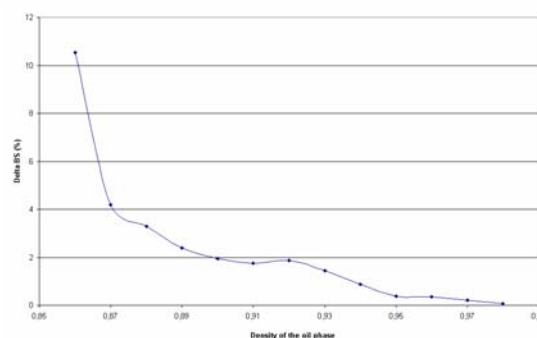


Figure 19. Effect of oil phase density on the ring formation.

We see on this graph that the density of the oil phase has a direct impact on the formation of the ring at the top of the drink. Indeed, by minimizing the density difference between both phases, the migration is significantly decreased⁷.

Conclusion

Therefore, we have shown that the Turbiscan® is a complete technique that can be used during all the development of a product from the formulation in the lab through the stability study to the production and the control of the quality of the products. It enables to measure stability of various types of beverage emulsions and to identify what sort of instability is taking place, even when several phenomena occur simultaneously or when nothing is visible to the eye. All the destabilisation can be analysed and followed separately using the different parameters available in the software. The overall stability study can be

shortened from 10 to 50 times, allowing quicker developments.

Moreover, the analyses can be accelerated and automated through the temperature increase and the use of the ageing station Turbiscan ags.

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