

# Physico-chemical separation process of nanoparticles in cosmetic formulations

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**Abstract.** Understanding the world of nanoparticles, especially their interactions with the environment, begins with their correct detection and successive quantification. To achieve this purpose, one needs to perform correctly developed standard operating procedures (SOPs). Furthermore, the study of nanoparticles frequently requires their characterisation in complex media (e.g. in cosmetic formulations). In this study, a set of sample preparation procedures for the detection and extraction of NMs in emulsion-based formulations is proposed and their performance for model and real-life products is discussed. A separation or extraction of lipid phases is achieved by means of organic solvents. The polarity of the lipid phases is decisive for selecting an optimum solvent. The use of the Hansen Solubility Parameters (HSP) may clearly support this decision.

**Keywords:** nanomaterials (NMs), Hansen Solubility Parameters (HSP), cosmetic formulations

## 1. Introduction

Nanomaterials (NMs) play an important role in the design of new products, since they allow for controlled variation of different product properties. This holds particularly true for cosmetic formulations and food products, where NM additives are employed as stabilisers, pigments, UV absorber, thickeners, flow enhancing agent and even more [1, 2]. Furthermore, there is potential concern on the health effects of NMs, because of which legal authorities request reliable methods for the characterisation of NMs in such products [3, 4]. Further motivations for appropriate characterisation techniques are process control and quality assurance.

This study proposes a set of sample preparation procedures for the detection of NMs in emulsion-based formulations and discusses their performance for model and real-life products [5]. One of these procedures is the extraction of lipid phases, which facilitates the characterisation of different NM polarities (e.g. hydrophobic or hydrophilic).



## 2. Materials and Methods

### 2.1. Methodological procedures

The present study focuses on SiO<sub>2</sub> based on its use in a wide range of consumer products – including cosmetics (hydrated silica) and foods (E551) – in form of powder, dilute liquid suspensions, emulsions or pastes [6]. Experiments were conducted for complex formulations, which were composed of aqueous solutions, dispersed lipid phases (24 wt.-%), hydrophobic fumed SiO<sub>2</sub> (10 wt.-%; BET 200 m<sup>2</sup>/g) and typical additives used in cosmetics (e.g. glycerol as thickening agent).

The qualitative analysis of particle size distribution (PSD) was conducted with scanning electron microscopy (SEM) – Gemini DSM 980 (Zeiss/Germany). The quantitative analysis of PSD was determined with standard analytical techniques (laser diffraction LD) – HELOS BR (Sympatec/Germany), dynamic light scattering (DLS) – HPPS (Malvern/UK), which are of low cost (compared to ICP-MS) and can quickly provide highly accurate results. However, when applied to specific particles in complex media they require appropriate preparation techniques and adopted measurement procedures [7]. Further problems arise since the dispersed phases typically cover a wide range of particle sizes (a few nanometres up to even millimetres).

### 2.2. Determination of size distribution

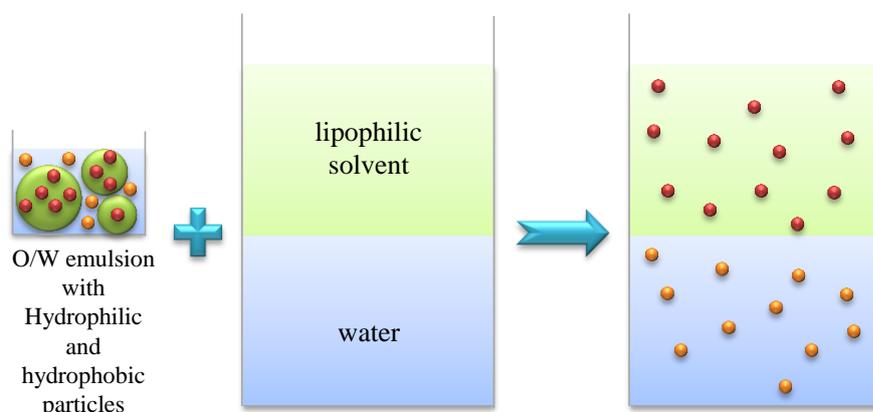
The selected methods for the determination of particle size distribution (PSD) are based on different measurands [8], i.e. equivalent diameters, and also on different types of quantity (e.g. DLS: intensity weighted) [9]. Furthermore, different size ranges are covered, each of which is smaller than the whole range from primary particle size to maximum agglomerate size. The detection, extraction and subsequent characterisation of NMs in multi-disperse systems as emulsions involve metrological difficulties [10]. This study discusses the development of preparation techniques for the adequate characterisation of silica particles in complex media. The characterisation of NMs in cosmetic formulations (e.g. Pickering emulsion) requires the appropriate development of SOPs for the preparation and extraction of NMs in dispersion systems. The structure of these SOPs can generally be classified into five steps, namely (1) wetting/suspending (polarity (hydrophobic and hydrophilic)), (2) dispersion (e.g. ultrasonic dispersion (cup horn, sonotrode and cleaning bath)), (3) sampling (mass/volume balance), (4) sample division/preparation (extraction, sedimentation/centrifugation), and finally (5) measurement/interpretation (e.g. particle size distribution (PSD)). The dispersion experiments can be quantitatively classified according to volume specific energy input.

## 3. Results – Characterisation of Cosmetic Emulsions

### 3.1. Evolution of separation and extraction process

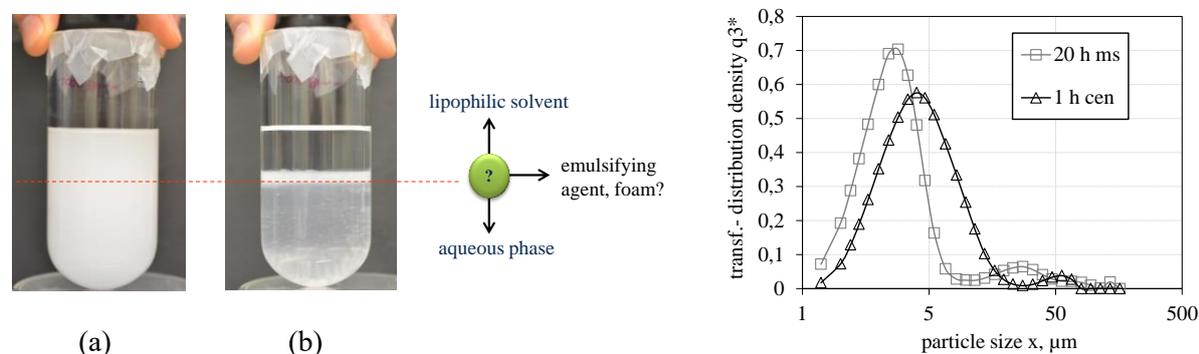
The characterisation of NMs in food and cosmetic emulsions is challenged by the presence of different liquid phases and the huge variety of solutes including rheological additives and amphiphilic molecules [11]. The different inorganic and organic solutes (e.g. electrolytes, sugar, emulsifiers, proteins) can significantly affect the interfacial properties of all particles (e.g. by adsorption/desorption) and thus influence the behaviour of the NMs in the product (dispersibility in aqueous and lipid phases, adsorption at fluid-fluid interfaces or on the surface of large particle).

A separation or extraction of lipid phases is achieved by means of organic solvents. The polarity of the lipid phases is decisive for selecting an optimum solvent. It can be shown that the use of the Hansen Solubility Parameters (HSP) may clearly support this decision [12, 13, 14, 15]. The principal idea consists in the separation of the oil droplets from the aqueous phase by means of bi-continuous mixtures of water with a lipophilic (i.e. non-polar) solvent (see Figure 1).



**Figure 1.** Proposal idea of the extraction process of solid particles of emulsion by means of bi-continuous mixtures of water with a lipophilic solvent

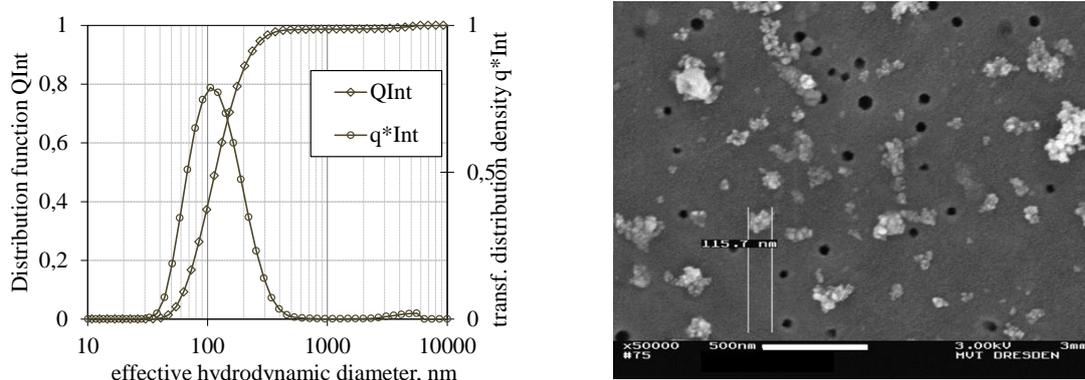
In this study, hydrophobic  $\text{SiO}_2$  was separated from oil droplets by dissolving the lipid in n-heptane and subsequent phase separation by centrifugation (see Figure 2). An emulsion sample of 1 g was added to 49.5 g water and 49.5 g heptane. The mixtures were then agitated by magnetic stirring for 20 hours. A preliminary test showed that this procedure leads to a stable mixture with slow phases separation under gravity. In order to work efficiently, the separation of selected bi-continuous mixtures of heptane and water was accelerated by centrifugation (see Figure 2).



**Figure 2.** Left: Hydrophobic fumed  $\text{SiO}_2$  in water and n-heptane (mixing ratio 1:1); (a) after 20 h magnetic stirring (ms), (b) after 1 hour centrifugation (cen) at 2600 g; Right: Change of size distribution (determined with LD) of a  $\text{SiO}_2$  cosmetic emulsion within water phase

After centrifugation one can observe three phases: the organic solvent, liquid foam with a high portion of emulsifying agent, and water. The solvent phase is transparent but contains solid nanoparticles as could be demonstrated with DLS and SEM analysis (see Figure 3).

The DLS indicates the existence of particles with the same size range as the  $\text{SiO}_2$  aggregates added to the emulsion. Moreover, SEM images impressively show the fractal morphology of particles in the n-heptane phase, which confirms that these particles present the hydrophobic fumed  $\text{SiO}_2$ . This proves the affinity of hydrophobic  $\text{SiO}_2$  in non-polar solution and supports the validity of the separation method.



**Figure 3.** Left: intensity weighted distribution for SiO<sub>2</sub> in n-heptane phase; Right: SEM image with high magnification (finest particles found); sample carrier: track-etch-membrane with 50 nm pore

#### 4. Summary and Conclusion

The detection of nanoparticulate material in complex media is not trivial. Common characterisation methods are focused particle systems with just one dispersed phase, preferably with low or moderate polydispersity. Therefore, it is very important, in such complex media, to implement adequate SOPs and to achieve objective interpretations of the analysis (PSD, equivalent diameters and also different types of quantity). This investigation verified an alternative procedure to separate particles with regard to the polarity of solvent and solute in complex cosmetic emulsions. This procedure is applicable to primary emulsion (e.g. O/W or W/O) or even secondary or multiple-emulsion (e.g. O/W/O or W/O/W) and it can be employed for hydrophilic as well as hydrophobic silica particles.

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