Characterization of Particle Properties

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Particle Characteristics:
Effect on Food Emulsion Properties

**Particle Properties**
- Particle concentration
- Particle size distribution
- Particle charge
- Interfacial properties
- Physical state

**Product Properties**
- Optical properties
- Rheology
- Stability
- Molecular distribution

**Product Performance**
- Appearance
- Texture
- Shelf Life
- Flavor
- Nutrition
Particle Characterization: Importance to Food Scientists

Quality Assurance
• To assure product meets specifications
  – Predict shelf life stability

Research and Development
• To understand relationship between product composition, processing conditions and quality

www.emulsifiers.org
Particle Characterization: Techniques & Protocols

Instrumental Techniques – actual instruments used to carry out measurements

- Microscopy
- Particle Sizing
- Particle Concentration Profiles

Experimental Protocols – methodologies used in laboratory to assess emulsion properties

- Storage Tests
- Accelerated Storage Tests
- Environmental Stress Tests
Microstructure & Particle Size

Microscopy Methods
- Optical
- Electron
- Atomic Force

- Particle Sizing Methods
- Light Scattering
- Electrical Pulse Counting
- Sedimentation
- Ultrasound, NMR

![Particle Size Distribution (PSD)](image)
Optical Microscopy

• Conventional Techniques
  – General Microstructure
  – Particle size

• Specialized Techniques (Dyes, Fluorescence, Polarization)
  – Ingredient location
  – Crystallization
  – Chemical reactions

Coarse Emulsion

Fine Emulsion

Lower Size Limit: $d > 0.5 \mu m$
Optical Microscopy:
Establishing Aggregation Mechanism

Casein Stabilized Emulsion

+ Pectin

pH 7
Flocculated

pH 6
Coalesced
Optical Microscopy:
Localization of Ingredients

- Salad dressing: DIC Phase Contrast
- Salad dressing: ANS-fluorescent stain for protein
- Salad dressing: Nile Red-fluorescent stain for fat

Courtesy of Kraft Foods
Optical Microscopy: Automated Image Analysis

1. Camera scanning
2. Image extraction
3. Segmentation
4. Result generation

Need large number of particles

Linear graticule
Logarithmic graticule

PSD
Optical Microscopy: Automated Image Analysis

- Particle Size, Shape & Aggr
- 0.5 to 1000 µm
- Automated, Rapid
- Emulsions, Powders

Takes multiple images and provides rapid analysis of particle characteristics
Electron Microscopy

TEM

- Obtain structural details on a very small scale (< 5 nm)
- Better for observing general structural features than for particle sizing
- Sample preparation is time-consuming & may alter structure
- Mainly used for research, rather than quality control

SEM

SEM of Microencapsulated fat
(CSIRO, Australia)

TEM of Vesicles
(www.steve.gb.com)
Electron Microscopy

SEM of Ice Cream
(Doug Goff, University of Guelph)

SEM of Emulsion
Royal Micro Soc.

TEM of Vesicles
(www.steve.gb.com)

SEM of Spray dried fat
(CSIRO, Australia)
Atomic Force Microscopy

- Obtain structural details on a very small scale (< 1 nm)
- Difficult to use for routine analysis
Particle Sizing Instruments

Advantages
• Automatic instrumental methods that can rapidly and precisely determine the full PSD of an emulsion

Disadvantages
• Do not directly observe emulsion microstructure
• Relatively expensive
• Sample preparation can be problematic

![Diagram showing particle size distribution over time]
Static Light Scattering

- **Principle:** Measure angular dependence of scattered light
- **Particle Size Range:** 50 nm – 1000 µm
- **Concentration Range:** < 0.1%

Laser

Light Detectors

Scattering Pattern

Theory

PSD

Volume% vs. Particle Diameter (µm)

0 2 4 6 8 10 12

0.01 0.1 1 10

Particle Diameter (µm)

I L S

φ
Data for Food Emulsions

PSD of Different Products

Mayonnaise
\( d_m = 6 \, \mu m \)

Cream Liqueur
\( d_m = 0.120 \, \mu m \)
Static Light Scattering
Importance of Sample Preparation

Factors Influencing Measurement:
- **Buffer properties (pH, I, T)**
- **Dilution**
- **Stirring**
- **Time**

Ensure Preparation Procedure is Appropriate!
Emulsion Drawn Through Tube

Light Obscuration Sensor

- **Principle:** Measures light obscuration as single particles passes through a small tube
- **Particle Size Range:** 0.5 – 5000 µm

Accusizer: Sci-Tec
Dynamic Light Scattering

- **Principle:** Measures rate of diffusion of particles via intensity fluctuations
- **Particle Size Range:** 1 nm – 6 µm
- **Concentration Range:** < 0.01 to >10%

Detector/Correlator

Laser

Brownian Motion

Malvern
Dynamic Light Scattering: Principles

Constructive Interference:
Bright Spot

Interference pattern depends on relative location of droplets
Dynamic Light Scattering: Principles

Destructive Interference: Dark Spot

Intensity vs. Time

Detector

Later time

Scattered waves

New Spatial Arrangement

Laser

Interference pattern depends on relative location of droplets

Brownian Motion
Dynamic Light Scattering

Small Particles

Large Particles

Analysis

$D \propto \frac{1}{\eta}$

PSD

$D \propto \frac{1}{\eta}$
Dynamic Light Scattering

Small Particles

Large Particles

Analysis

PSD

$D \propto 1/\eta$

Time

Intensity

$0 10 20 30$

$0 2 4 6 8 10 12$

Time

Intensity

$0 10 20 30$

$0 2 4 6 8 10 12$
Data for Food Emulsions

Effect of Homogenization on Ice Cream

Increasing homogenization pressure

% in class

5 10

5 10

Diameter (nm)
Dynamic Light Scattering
Formation of Nanoemulsions

Surfactant (wt%) vs Diameter (nm)

-TAG High η
-Tag Low η

Alkane Low η
Diffusion Microscopy
Particle Movement Tracker

Darkfield microscopy image of particles: Video tracking of particles moving through Brownian motion gives particle size distribution

D = 10 – 1000 nm
Electric Pulse Counting
(Coulter Counter)

- **Principle:** Measure change in electrical current as droplet passes through a small hole
- **Particle Size Range:** 0.4 – 100 µm
- **Concentration Range:** < 0.1%

Elzone: Micromeritics

Coulter-Counter: Beckman-Coulter
**Sedimentation/Creaming**

Gravitational or Centrifugation

- **Principle:** Measure change in droplet concentration with sample height and time
- **Particle Size Range:** 40 nm – 1000 µm
- **Concentration Range:** Depends on method

Lumisizer: LUM
**Principle:** Measure change in ultrasonic attenuation coefficient with frequency

**Particle Size Range:** 0.1 – 1000 µm

**Concentration Range:** Up to 50%
**NMR - Restricted Diffusion**

- **Principle:** Measure distance moved by dispersed phase molecules in specified time
- **Particle Size Range:** 0.5 – 1000 µm
- **Concentration Range:** Up to 80%

*Image of NMR equipment*
Factors to Consider when Purchasing PSD Equipment

Particle Characteristics
- **Size Range:** nm to µm
- **Concentration Range:** Dilute – Concentrated
- **Organization:** Droplets or Flocs

Sample Characteristics
- **Physical State:** Solid, Liquid, Powder
- **Optical:** Transparent or Opaque

Destructive/Non-destructive
- In-Line or Bench-Top

Cost
- $5K to $150K

Ease of Use
- Manual or Automatic
- Measurement Speed
Selecting a Particle Size Analyzer

Is the sample solid or liquid?

Optically Transparent
- Dilute/Dilutable

Small → DLS, EM

Large → SLS, EPC, S, OM

Optically Opaque
- Concentrated

Small → DLS, US, EM

Large → US, NMR, OM

Is the sample opaque or transparent?

Are the particles small (< 0.4 µm) or large (> 0.4 µm)?

Optically Transparent
- Dilute

Small → EM

Large → SLS, OM

Optically Opaque
- Concentrated

Small → US, EM

Large → US, NMR, OM

Solid

Microscopy
Optical (OM)
Electron (EM)

Particle Analyzers
SLS
DLS
Pulse Counting (EPC)
Sedimentation (S)
NMR
Ultrasound (US)
# Comparison of Commercial Particle Size Analyzers

<table>
<thead>
<tr>
<th>Technique</th>
<th>$r$ Range</th>
<th>$\phi$ Range</th>
<th>Comments</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microscopy</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Optical</td>
<td>&gt; 0.5 µm</td>
<td>0.1 – 50%</td>
<td>ND, SP, Slow</td>
<td>$5 – 25 k$</td>
</tr>
<tr>
<td>Electron</td>
<td>&gt; 5 nm</td>
<td>0.1 – 50%</td>
<td>D, SP, Slow</td>
<td>&gt;$100 k</td>
</tr>
<tr>
<td>Particle Analyzers</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>SLS</td>
<td>50 nm – 1000 µm</td>
<td>&lt; 0.1%</td>
<td>D, SP, Fast</td>
<td>$30 – 60 k$</td>
</tr>
<tr>
<td>DLS</td>
<td>3 nm - 5 µm</td>
<td>0.1 – 30%</td>
<td>D, SP, Fast</td>
<td>$30 – 60 k$</td>
</tr>
<tr>
<td>Pulse Counting</td>
<td>400 nm - 100 µm</td>
<td>&lt; 0.1%</td>
<td>D, SP, Fast</td>
<td>$30 – 50 k$</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>100 nm - 100 µm</td>
<td>Depends</td>
<td>D, SP, Fast</td>
<td>$30 – 50 k$</td>
</tr>
<tr>
<td>NMR</td>
<td>500 nm - 100 µm</td>
<td>1 – 60%</td>
<td>ND, NSP, Fast</td>
<td>$80 – 150 k$</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>10 nm - 1000 µm</td>
<td>1 – 50%</td>
<td>ND, NSP, Fast</td>
<td>$50 – 90 k$</td>
</tr>
</tbody>
</table>

ND/D = Non-Destructive/Destructive
NSP/SP = No Sample Preparation/Sample Preparation
Other Factors
Reporting Particle Sizes Correctly

Size: Diameter or Radius?
Concentration: Number or Volume?
Representation: Mean Size or Full Distribution?
Type: Droplets or Flocs?
Experimental Protocols: Testing Emulsion Stability

- **Storage Tests**: Mimic normal product storage conditions
- **Accelerated Storage Tests**: Predict long-term stability by speeding up breakdown (e.g., centrifugation, heating, shaking)
- **Environmental Stress Tests**: Establish ability of emulsions to resist specific stresses

Does accelerated stress test mimic long-term storage test?
Experimental Protocols:
Stability to Environmental Stress

Minerals and pH
- pH 2 to 8
- NaCl 0 – 1 M, CaCl₂ 0 – 100 mM

Thermal Processing
- 30-90 ºC for 30 minutes

Freeze Thaw Cycling
-20ºC / +20ºC

Dehydration
- Spray drying or Freeze drying

Mechanical Agitation
- Shaking, Stirring

Measure:
- Microscopy
- PSD
- Creaming
- Rheology
Experimental Protocols
Testing Emulsion Stability

Identify Mechanism!

Flocculation
Stable Emulsion
Coalescence or OR
Gravitational Separation
Phase Separation
Experimental Protocols: Establishing Aggregation Mechanism

**Flocculation**
- Direct observation of microstructure by microscopy
- Particle size decreases after adding deflocculant

**Coalescence**
- Direct observation of microstructure by microscopy
- Measure evolution of PSD with time
- Bimodal distribution formed
- Particle size unchanged after adding deflocculant

**Ostwald Ripening**
- Observe microstructure by microscopy
- Measure evolution of PSD with time
- Remains as monomodal distribution
- Droplet growth rate proportional to $r^3$
- Particle size unchanged after adding deflocculant

![Graph showing particle diameter vs. volume percentage for 0 mM NaCl and 150 mM NaCl](image)
Conclusions

• A wide variety of analytical instruments are now available for emulsion characterization
• The choice of a particular instrument depends on the food material being tested and the information required
• A robust testing protocol should be developed to identify instability mechanisms and/or to monitor product quality
• Clear product particle size distribution specifications should be established