Food Structure

Volume 12 | Number 2 Article 10

1993

The Surface Coverage of Fat on Food Powders Analyzed by Esca (Electron Spectroscopy for Chemical Analysis)

Pia Faldt

Bjorn Bergenstahl

Gilbert Carlsson

FOOD STRUCTURE, Vol. 12 (1993), pp. 225-234
Scanning Microscopy International, Chicago (AMF O'Hare), IL 60666 USA

1046-705X/93$5.00+.00

THE SURFACE COVERAGE OF FAT ON FOOD POWDERS ANALYZED BY ESCA (ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS)

Pia Fäldt, Björn Bergenståhl and Gilbert Carlsson

Institute for Surface Chemistry,
P.O. Box 5607, S-114 86 Stockholm, Sweden

Abstract

ESCA (electron spectroscopy for chemical analysis) was used to estimate the fat coverage on different spray-dried food powder surfaces. The method presented here represents a new way of estimating the actual surface coverage of fat on a food powder. The ESCA-method is illustrated with three different series of experiments. The results obtained with the ESCA-technique are combined with the results obtained from the conventional free fat extraction technique for different spray-dried powders.

In the first series, emulsions containing different ratios of protein to fat were spray-dried. An increase in the amount of fat in the emulsion gives an increased surface coverage of fat. Powders with a high fat content shows a high free fat level, indicating a continuous network of fat inside the particles.

Secondly, the effect of heat treatment on the ability of bovine serum albumin to encapsulate fat has been investigated. The results show that albumin treated at high temperature encapsulates the fat less completely than the albumin treated at low temperature.

Finally, emulsions containing oil phases with different melting points were spray-dried and analyzed. Powders with a high melting fat show very well encapsulated fat with only a minor surface coverage of fat. Powders with a qualitatively different distribution of fat can be identified by comparing the surface coverage of fat estimated by ESCA with the free fat measurements.

Key Words: Food powders, surface fat, free fat, ESCA, emulsion, spray-drying, fat distribution, sodium caseinate, surface analysis, powder properties.

Initial paper received December 15, 1992
Manuscript received April 26, 1993
Direct inquiries to P. Fäldt
Telephone number: 46-8-790 99 00
Fax number: 46-8-20 89 98

Introduction

The presence of fat on a food powder surface is a critical parameter for the quality of the powder. The fat is, in most cases, the powder component which is most sensitive to oxidation, and it should therefore be protected from oxygen in the air. Since surface fat makes the powder more hydrophobic, it leads to a deterioration in the wettability and dispersibility of the powder in water. A high surface fat content is, therefore, undesirable in food powders for household use, although it is important for the functionality of whole milk powder used in several industrial applications, for example, in the chocolate industry (Pisecky, 1986). It is, therefore, desirable to be able to control the amount of surface fat when food powders are made.

Free fat, defined as the amount of fat that can be extracted from food powders by an organic solvent, is an important parameter used to characterize fat-containing food powders. The free fat is supposed to represent the fat present on the surface of the powder, although it has been established several times that the free fat originates not only from the surface of the food powder, but also from the interior of the particles (Buma, 1971a-h; De Vilder *et al.*, 1977; Buchheim, 1982). The organic solvent can reach the interior through cracks and pores in the particles. Buma (1971a-h) investigated the free fat content in detail in relation to the powder properties, and proposed a model where the free fat consists of four different types: f_s = surface fat, f_l = outer layer fat from fat globules in the surface layer of the particle, f_c = capillary fat consisting of fat globules inside the particle which can be reached by fat solvents via capillary pores or cracks, and f_d = dissolution fat consisting of fat globules which can be reached by the solvent through holes left by already extracted globules. The model was confirmed qualitatively by electron microscopic studies by Buchheim (1982).

It has not however been possible to distinguish quantitatively between the different types of free fat. With this in mind, a technique has now been developed for the direct determination of the surface fat on powders using a surface analyzing technique, ESCA (electron spectroscopy for chemical analysis). These

measurements are expected to show the surface coverage of fat on the particles.

The experiments presented below illustrate the behaviour of powders of different origins and characters.

Materials and Methods

Materials

Spray-dried sodium caseinate, Miprodan CW, was obtained from MD Foods, Denmark. The sodium caseinate contained 94.5% protein and 1% fat. Partly hydrogenated coconut oil [melting point, mp 33°C] and partly hydrogenated rapeseed oil, Lobra 34 [mp 20-40°C], were obtained from Karlshamns AB, Sweden. Tristearin, puriss [mp 73°C] was obtained from Fluka AG, Switzerland. Bovine serum albumin, fraction V, 96-99% (Sigma Chemicals) was obtained from Lab Kemi, Sweden.

Preparation of emulsions

Before the homogenization the emulsions were prehomogenized in a high speed colloid mill, Ultra turrax [IKA, Germany] at 24,000 rpm for 2 minutes. The emulsions were then homogenized in a high pressure homogenizer, microfluidizer, TM-110 [Microfluidics Inc., Newton, Mass., USA] at 1000 bar. Each emulsion was recycled approximately five times. The particle size of the emulsions before spray-drying for two of the experimental series are shown in Tables 1 and 2.

Sodium caseinate/coconut oil emulsions

The solids content of the emulsions was 20%. The ratio of coconut oil to sodium caseinate varied between 0.2 and 0.9. The emulsions were homogenized at 40°C.

Sodium caseinate/oil emulsions

The emulsions contained sodium caseinate and an oil phase with different melting points. The fat phases were: soybean oil (mp ≈ -20°C), hardened coconut oil (mp 33°C), partially hardened rapeseed oil (mp 20-40°C) and tristearin (mp 73°C). The solids content of the emulsions was 10%. The ratio of fat to sodium caseinate was 1:1. The homogenization was carried out at 75°C.

Bovine serum albumin (BSA) / soy bean oil emulsions

The BSA solutions were heat treated for 5 minutes in a water bath at different temperatures between 20 and 95°C. The BSA-solution was then mixed with soy bean oil and homogenized at 20°C.

The solids content of the emulsions was 10%. The ratio of BSA to soy-bean oil was 1:1 for all emulsions prepared.

Determination of the droplet size in the emulsion

The size of the oil droplets in the emulsions was measured using laser light diffraction. The instrument used (Malvern Mastersizer, Malvern Instruments, Malvern, England) employs a modified Mie-scattering model to estimate the droplet size.

Table 1. Particle size for emulsions with different fat phases

Fat phase	Melting point of the fat [°C]	d (4,3) [μm]
Soybean oil	-5	0.34
Coconut oil	33	0.42
Rapeseed oil	20-40	0.34
Tristearin	75	0.28

Table 2. Particle size for heat-treated BSA stabilized emulsions.

Heat-treatment temperature of BSA [°C]	d (4,3) [μm]
20	6.85
50	4.54
65	3.38
80	6.57
95	10.38

Spray-drying of the emulsions

The emulsions were spray-dried in a laboratory spray dryer built at the Institute for Surface Chemistry. The dimensions of the drying chamber are 0.5 x 0.15 m. The spray-dryer operates co-currently which has a spray-nozzle with an orifice with a diameter of 1 mm. The inlet gas temperature was 180°C for all the emulsions investigated. The outlet gas temperature was 110°C for the sodium caseinate/coconut oil emulsions, and 80-90°C for the other two emulsion types, except for one emulsion containing tristearin where the outlet temperature was held at 65°C, i.e., below the melting point of the tristearin. The liquid feed to the dryer was ≈ 11 ml/min. The flow of drying air was ≈ 0.8 m^3/min.

ESCA-measurements

The ESCA measurements were made with a PHI 5000 LS (Perking-Elmer, USA) at Kabi-Pharmacia AB in Uppsala, Sweden. The instrument used a monochromatic Al Kα X-ray source. The pressure in the working chamber during the analysis was less than $1x10^{-7}$ torr. The instrument worked with a spherical capacitor analyzer. The take-off angle of the photoelectrons was 45°. The analyzer operated with a pass energy of 71.55 eV. The step size was 0.2 eV. The spectra acquisition time varied depending on the peak area. The analyses were performed the day after the emulsions were dried to avoid oxidation of the powder. The powders were spread on the surface of the sample holders without mounting when the ESCA-analysis was carried out. The analyzed area of the powder was 1 x 3.5 mm.

Free-fat extraction

The free fat extraction was made with petroleum ether (boiling point, bp 65-75°C) according to the Niro

Atomizer Method No A 10 a with some modifications, (A/S Niro Atomizer, 1978). One gram of the powder was added to 6 ml of dried petroleum ether, and shaken for two minutes. The solvent was first separated by filtration. The filtrate solution containing the extracted fat was then allowed to evaporate until the extracted fat residue achieved a constant weight. The free fat value is here defined as gram extractable fat/gram powder.

Scanning electron microscopy (SEM)

The samples were mounted on a double-sided sticky tape attached to SEM-stubs. The powders were covered with gold by a diode sputter, Balzers Union AG. The samples were examined with a Philips SEM 515 operating at 15 kV.

ESCA Characterization of Food Powders

Basic principles of ESCA

Electron Spectroscopy is a well-established technique for the analysis of solid surfaces. The sample to be analyzed is exposed to an X-ray beam ($h\nu$) see Fig. 1. Electrons with a binding energy (E_b) less than the photon energy ($h\nu$) will be ejected from the atom. The kinetic energy of the ejected electron (E_k) will be approximately equal to the difference between the photon energy and the binding energy. The basic equation for ESCA is:

$$E_k = h\nu - E_b - \phi \qquad [1]$$

where ϕ is the instrument work function. Because the binding energy is characteristic of the atom from which it is ejected, it is possible to identify the elements present in the specimen. The composition can be quantified using the appropriate sensitivity factors (Briggs and Seah, 1990).

The electrons emitted from the sample originate from the near surface region of most solids ($\approx$ 10 nm). The surface sensitivity of ESCA is due to the inelastic scattering of the photoelectrons with the solid matter. In this process, electrons located far from the surface lose energy and end up as background intensity. The electrons that succeed in escaping from the surface thus originate from a very thin layer close to the surface. To avoid further scattering, the analysis has to be performed in ultra-high vacuum, 10^{-8} torr.

The amount of electrons contributing to the signal will decay with increasing distance z from the surface of the material for flat specimens according to:

$$I(z) = I(0)\exp(-z/\lambda \sin \alpha) \qquad [2]$$

which is shown in Fig. 2. I(0) is the intensity at z = 0, λ is the attenuation length which is different for different elements and materials and α is the analyzer take-off angle. The attenuation length, λ [in Å] can be estimated for different organic polymers according to the model developed by Ashley (1980):

$$\lambda = \{(M/\rho n)E_k\} / (13.6 \ln(E_k) - 17.6 - 1400/E_k) \qquad [3]$$

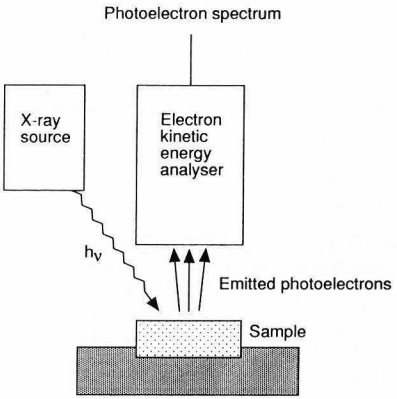

Figure 1. The principle of ESCA (electron spectroscopy for chemical analysis).

Table 3. λ-values for albumin and coconut oil.

	λ [in nm]		
	C 1s	O 1s	N 1s
Albumin	3.5	2.9	3.2
Coconut oil	3.8	3.3	3.6

where M is the molecular weight of the molecule or repeat unit [g/mole], n is the number of valence electrons in the repeat unit, σ is the density [g/cm^3] and E_k is the kinetic energy of the electrons [eV]. Values of λ for different elements in albumin and coconut oil are shown in Table 3. The values for the fat have been calculated using equation [3]. The other λ-values are taken from Andrade (1985).

In cases where the surface layer is very thin ($< 3\lambda$), the underlying material contributes to the signal (Fig. 3). Equation [2] holds for flat surfaces. For spherical particles, equation [2] has to be modified. An approximate estimation of the enhanced surface sensitivity of the analysis of spherical particles can be done as follows. If the distance between the detector and the sample is long compared to the radius of the particles; and, if the emitted electrons are scattered randomly from the surface with a certain depth for emission, the emission from the particles will be equal to the emission from a two-dimensional projection of the particles, a round flat plate. The apparent emission angle (α) of the emitted electrons determining the analytical depth will depend on the distance l from the center of the plate having radius r:

$$\alpha = \arccos(l / r) \qquad [4]$$

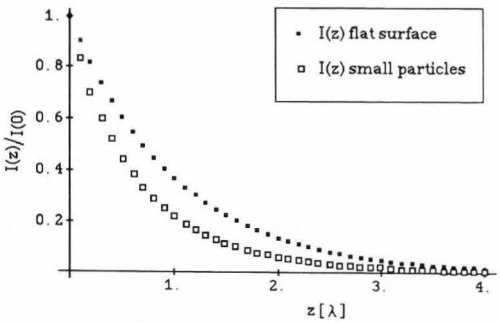

Figure 2. The depth of information from the ESCA-signal.

The emitted radiation I(z) as a function of l is obtained from eqs. [2] and [4]:

$$I(z,l) = I(0)(1/\exp[z/\{\lambda \sin(\arccos(l/r)\}] \quad [5]$$

The average emitted radiation from the whole plate is:

$$I(z) = \frac{1}{A}\int_0^{\Lambda} I_{(z,l)} dA = \frac{1}{\pi r^2}\int_0^{r} I_{(z,l)} 2\pi l dl \quad [6]$$

If a dimensionless distance from the center l′ = l/r is used, the equation reduces to:

$$I(z) = \int_0^1 I_{(z,l')}\, 2l' dl' \quad [7]$$

The integration must be performed numerically. It shows that an underlying layer contributes even less to the signal for a spherical particle than for a flat surface. Figure 2 shows how the contribution to the signal from an underlying protein layer depends on the thickness of the fat layer for a flat surface and for a spherical particle.

The calculations show that for a spherical particle, an underlying layer will not contribute to the signal as long as the surface layer is thicker than 2 λ, which is equivalent to ≈ 8 nm.

The following calculations assume that t > 2λ, i.e., the underlying layer does not contribute to the signal. According to the electron microscopic information, this is the most probable situation for fat layers (Buchheim, 1982). This is also the case for multilayers of protein. Monolayers of protein can be expected to be in the range of 3-5 nm.

Analysis of food powders

Each component in the powder is characterized by the specific ratio between the elements. From an analysis of the relative amounts of the different elements in the pure components and in the pôwder, it is possible to

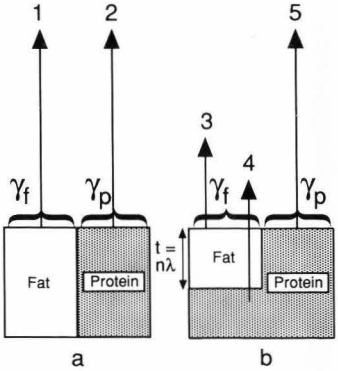

Figure 3. Illustration of the signal achieved from powders: **a**. thick fat layers; **b**. thin fat layers with thickness, t = nλ.

---

estimate the percentage of the powder surface which is covered with fat. The surface composition can thus be quantified.

If a particle comprises *i* components, an estimate of the relative coverage of these components requires at least *i* elements in the sample. The elements are denoted by *n*. The relative amount of the element *n* in the pure component *i* is denoted $I^n_{comp.i}$. The relative amount of element *n* in the sample is denoted I^n_{sample}. The relative coverage of component *i* is expressed as γ_i, and the relative coverage of the different components is expressed by a matrix formula:

$$\begin{pmatrix} I^1_{comp.1} & \cdots & I^1_{comp.i} \\ \vdots & & \vdots \\ I^n_{comp.1} & \cdots & I^n_{comp.i} \end{pmatrix} \cdot \begin{pmatrix} \gamma_1 \\ \vdots \\ \gamma_i \end{pmatrix} = \begin{pmatrix} I^1_{sample} \\ \vdots \\ I^n_{sample} \end{pmatrix} \quad [8]$$

or

$$\mathbf{I}_{comp} \cdot \gamma = \mathbf{I}_{sample} \quad [9]$$

The equation is solved by:

$$\mathbf{I}_{sample} \cdot \mathbf{I}^{-1}_{comp} = \gamma \quad [10]$$

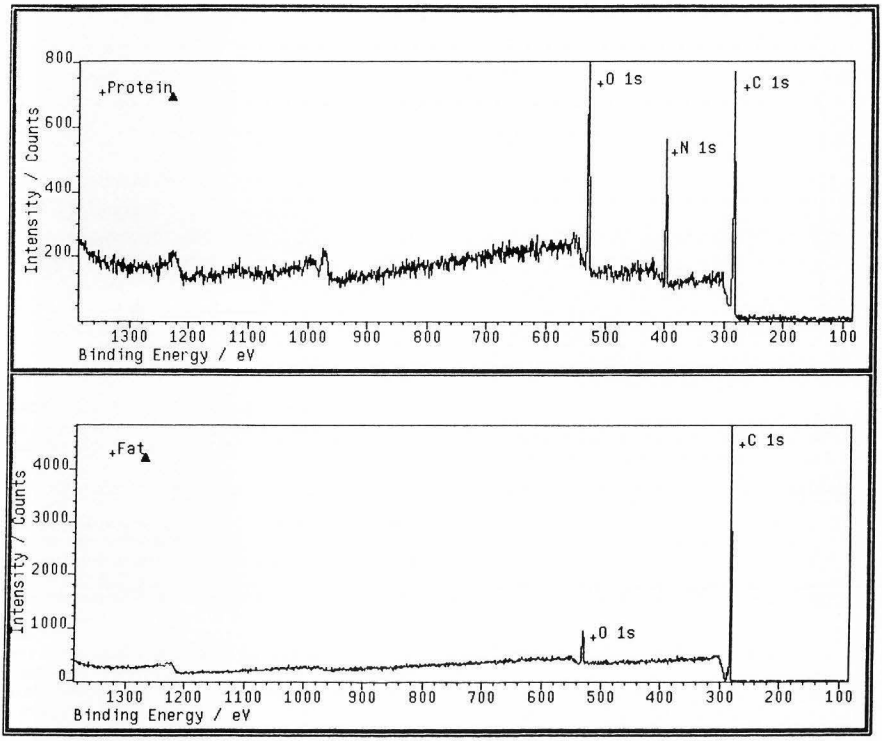

Figure 4. Survey spectra of protein and fat.

In this particular case, we consider a food powder made up of fat and protein. The spectra of the pure components of which the powders are made are shown in Figure 4. The fat contains carbon and oxygen, and the protein contains carbon (C), oxygen (O) and nitrogen (N). The relative amount of element n from the components are designated I_p^n for the protein and I_f^n for the fat.

For each of the elements: C, O, N, in the final powder, the relative amount can be expressed as:

$$I^C_{sample} = I^C_f \cdot \gamma_f + I^C_p \cdot \gamma_p \quad [11]$$

$$I^O_{sample} = I^O_f \cdot \gamma_f + I^O_p \cdot \gamma_p \quad [12]$$

$$I^N_{sample} = I^N_f \cdot \gamma_f + I^N_p \cdot \gamma_p \quad [13]$$

Where I^C_{sample}, I^O_{sample}, and I^N_{sample}, are the relative amounts of carbon, oxygen and nitrogen in the sample, γ_f is the fraction of the area covered with fat and γ_p is the fraction of the area covered with protein. In this particular case, the matrix is overestimated and was solved by the least squares method.

Reproducibility of the ESCA-measurements

ESCA-measurements performed on an homogeneous powder such as pure sodium caseinate make it possible to estimate the standard deviation, σ_{n-1}, in the ESCA signals for powders. The following results have been obtained for pure sodium caseinate from six independent measurements (relative atomic concentration, in %): C: 66.8 ± 0.7; O: 18.1 ± 0.2; and N: 15.1 ± 0.5.

In the spray-dried powder samples there are inhomogeneities within the powder which contribute to variations between the measurements.

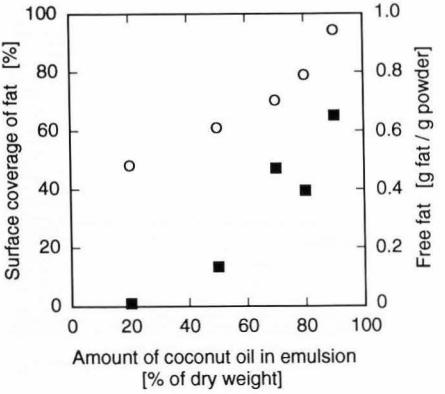

Figure 5. The surface coverage of fat from ESCA-measurement and free fat as a function of the ratio of coconut oil to sodium caseinate in spray-dried emulsion. ○ surface coverage of fat (%), ■ free fat (g fat/g powder).

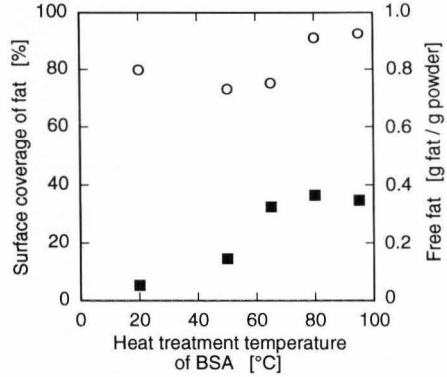

Figure 7. The surface coverage of fat from ESCA-measurement and free fat as a function of the heat-treatment temperature of bovine serum albumin (BSA). ○ surface coverage of fat (%), ■ free fat (g fat/g powder).

Results

Sodium caseinate/coconut oil emulsions

Emulsions with different ratios of sodium caseinate to coconut oil have been spray-dried and characterized. Figure 5 shows the amount of surface fat on the

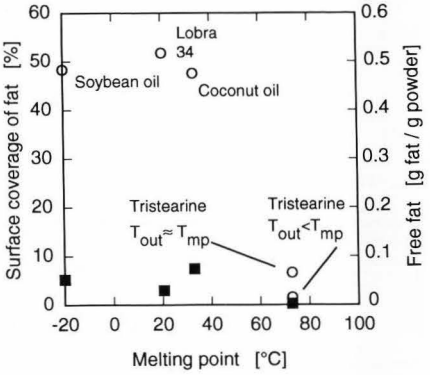

Figure 6. The surface coverage of fat from ESCA-measurement and free fat as a function of melting point of the fat phase. ○ surface coverage of fat (%), ■ free fat (g fat/g powder).

powder, as estimated by ESCA, compared with the amount of free fat in the emulsions with different fat/protein ratios. The amount of fat on the surface increases with increasing fat/protein ratio in the emulsion. The surface fat estimated by ESCA is a direct measure of the surface coverage of fat on the powder, the free fat measures only the amount of extractable fat from the powder, which does not necessarily originate from the surface. For the powders which contain a low amount of fat, there is an obvious difference between the surface fat estimated with ESCA and the free fat. The difference indicates that the fat layer on the powder surface is thin in this case, since 50% of the surface is covered with fat, but only a small amount of fat is extracted ≈ 0.04 g fat extracted/g powder. For powders with a higher fat content, the surface fat coverage is high and so also is the free fat. This indicates a thicker fat layer on the surface and/or that fat inside the particles is accessible to the solvent when it is extracted.

Different melting points of the oil phase

Figure 6 shows the surface coverage of fat on the powders as a function of the melting point of the fat. The powders were made from emulsions stabilized with sodium caseinate. The results show that the powders made with low melting fat and fat having intermediate melting points have a fat coverage of about 50%. Powders made of high melting fat, e.g., tristearin exhibit good encapsulation of the fat. In this set of experiments, the dryer had an outlet temperature of approximately 70°C. Hence, the tristearin was never melted during the drying. That the crystalline tristearin was then unable to spread over the powder surface during the

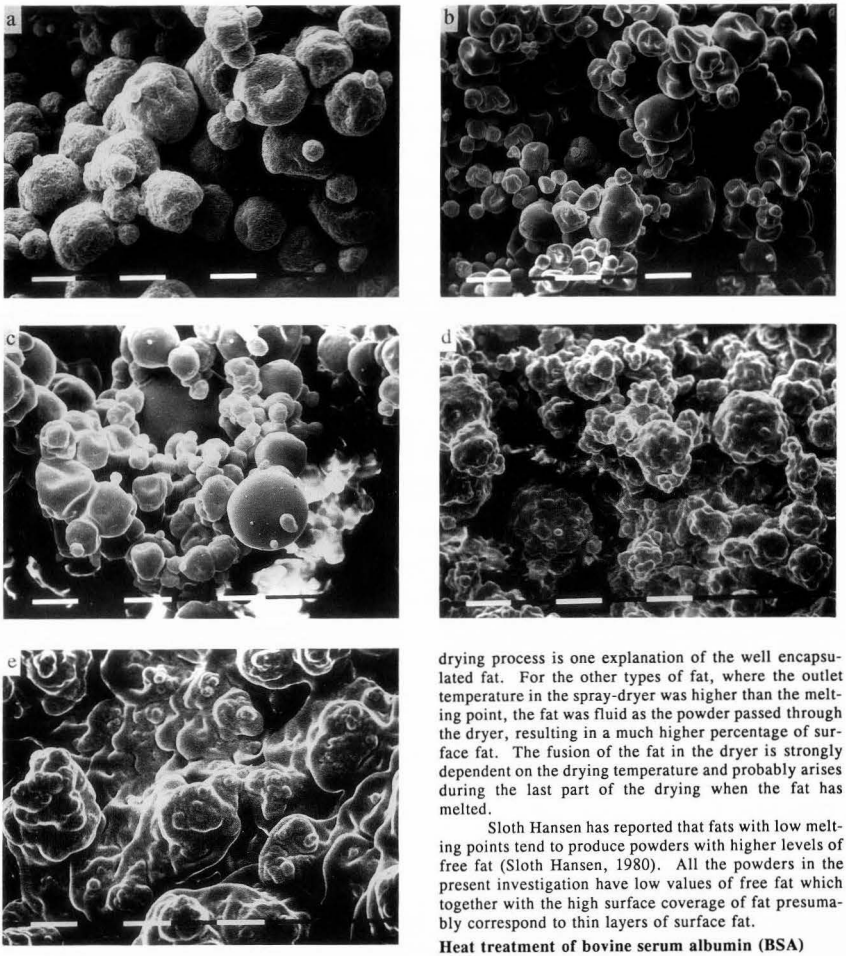

Figure 8. Powders made from soy-bean oil emulsions stabilized with BSA heat-treated at different temperatures: **a.** 20°C, **b.** 50°C, **c.** 65°C, **d.** 80°C, and **e.** 95°C. Bar = 10 μm.

drying process is one explanation of the well encapsulated fat. For the other types of fat, where the outlet temperature in the spray-dryer was higher than the melting point, the fat was fluid as the powder passed through the dryer, resulting in a much higher percentage of surface fat. The fusion of the fat in the dryer is strongly dependent on the drying temperature and probably arises during the last part of the drying when the fat has melted.

Sloth Hansen has reported that fats with low melting points tend to produce powders with higher levels of free fat (Sloth Hansen, 1980). All the powders in the present investigation have low values of free fat which together with the high surface coverage of fat presumably correspond to thin layers of surface fat.

Heat treatment of bovine serum albumin (BSA)

The effect of heat treatment of the protein before emulsification was investigated in a BSA/soy bean oil emulsion. The surface coverage of fat and the free fat are shown in Fig. 7 as a function of the heat treatment temperature of the protein. BSA is a small hydrophobic protein with acceptable emulsifying properties (Tornberg *et al.*, 1990), even though the particle size is much larger in emulsions stabilized with BSA than in emulsions stabilized with caseinate, Tables 1 and 2. The

treatment of BSA at high temperature leads to denaturation of the protein and gives a coarser emulsion. The particle size increases from approximately 4 μm up to 10 μm for the BSA treated at 20 and 95°C respectively, see Tables 1 and 2.

In general, the BSA stabilized emulsions have a high surface coverage of fat. For the samples with BSA treated at low temperatures the free fat content is low, indicating a thin surface fat layer. Treating BSA at a temperature of 40-60°C results in powders with a totally different appearance than that of a sample treated at 20°C, see Figures 8a-c. The surface fat is almost the same as in the sample treated at the lower temperature, but the fact that the free fat is greater suggests thicker fat layers or a coarser powder with fat in the interior accessible to the solvent. The samples treated at high temperatures, 80-90°C, have a comparatively high amount of free fat and also a very high surface coverage of fat. The fat in these powders is thus poorly encapsulated. Scanning electron micrographs of the high temperature treated BSA-samples, Figures 8d-e show a highly agglomerated powder.

Discussion

The method here described provides new possibilities of directly measuring the actual fat coverage on powder surfaces. The free fat extraction method, which is often used, gives only indirect information. By combining these two methods and electron microscopy, qualitative information relating to fat layer thickness, actual coverage of fat, particle morphology, etc. is achieved. Fig. 9 shows how the combination of free fat and surface fat displays the differences in character between different powders. Three different characteristics of the fat distribution in the powders can be distinguished:

1. Samples with a high degree of encapsulation: low free fat value and low surface coverage of fat. The powder made from the high melting tristearin dispersion shows an exceptional encapsulation.

2. Samples with fat released at the surface, but a well encapsulated fat in the interior: low free fat values but high surface coverage of fat. Typical examples are the BSA emulsions treated at low temperatures and the low fat-containing caseinate emulsions. The powders probably have a structure with separate fat pools in the interior and with the surface covered with a layer of fat.

3. Samples showing a poor encapsulation of the fat: high free fat values and a high surface coverage of fat. Examples are the BSA-samples temperature treated at high temperature and the high fat caseinate samples. These powders have a layer of fat on the surface and probably a more or less continuous internal fat phase.

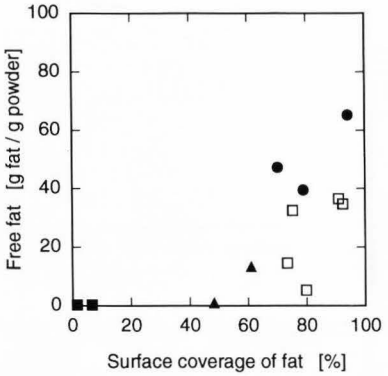

Figure 9. The relation between surface fat determined by ESCA-measurement and free fat for different types of powders. □ BSA stabilized emulsions, fat content 50% (dry weight); ● caseinate stabilized emulsions, high fat content, 70, 80, 90% (dry weight); ▲ caseinate stabilized emulsions, low fat content, 40, 20% (dry weight); ■ Caseinate stabilized emulsion, high melting fat, fat content 50% (dry weight).

Acknowledgement

The authors thank the Swedish Council for Forestry and Agricultural Research (SJFR) for financial support. Further thanks are extended to Mr. Anders Svensk, Mrs. Ann Setterquist, Ms. Rebecca Silveston, Institute for Surface Chemistry and to John Bristow for assistance in the preparation of this manuscript. Finally, we thank Mr Åke Öhrlund, Kabi-Pharmacia AB, Uppsala for performing the ESCA-measurements.

References

Andrade JD. (1985). X-ray photoelectron spectroscopy (XPS). In: Surface and Interfacial Aspects of Biomedical Polymers, Volume 1. Andrade JD (ed.), Plenum Press, 105-195.

A/S Niro Atomizer. (1978). Analytical methods for dry milk products. 4th Ed. A/S Niro Atomizer, Søborg, Denmark.

Ashley JC. (1980). Inelastic interactions of low-energy electrons with organic solids: Simple formulae for mean free paths and stopping powers. IEEE Trans. Nucl. Sci. **NS-27**, 1454-1458.

Briggs D, Seah MP. (eds.). (1990) Practical Surface Analysis. 2nd Ed. Volume 1: Auger and X-ray Photoelectron Spectroscopy. Wiley. pp. 635-638.

Buchheim W. (1982). Electron microscopic localization of solvent-extractable fat in agglomerated spray-

dried whole milk powder particles. Food Microstruc. **1**, 233-238.

Buma TJ. (1971a). Free fat in spray-dried whole milk. 1. General introduction and brief review of literature. Neth. Milk Dairy J. **25**, 33-41.

Buma TJ. (1971b). Free fat in spray-dried whole milk. 2. An evaluation of methods for the determination of free-fat content. Neth. Milk Dairy J. **25**, 42-52.

Buma TJ. (1971c). Free fat in spray-dried whole milk. 3. Particle size. Its estimation, influence of processing parameters and its relation to free-fat content. Neth. Milk Dairy J. **25**, 53-72.

Buma TJ. (1971d). Free fat in spray-dried whole milk. 4. Significance of free fat for other properties of practical importance. Neth. Milk Dairy J. **25**, 88-106.

Buma TJ. (1971e). Free fat in spray-dried whole milk. 5. Cohesion; determination, influence of particle size, moisture content and free-fat content. Neth. Milk Dairy J. **25**, 107-122.

Buma TJ. (1971f). Free fat in spray-dried whole milk. 8. The relation between free-fat content and particle porosity of spray-dried whole milk. Neth. Milk Dairy J. **25**, 123-140.

Buma TJ. (1971g). Free fat in spray-dried whole milk. 9. The size distribution of fat globules in concentrated milk and in spray-dried milk. Neth. Milk Dairy J. **25**, 151-158.

Buma TJ. (1971h). Free fat in spray-dried whole milk. 10. A final report with a physical model for free fat in spray-dried milk. Neth. Milk Dairy J. **25**, 159-174.

De Vilder J, Moermans R, Martens R. (1977). The free fat content and other physical characteristics of whole milk powder. Milchwissenschaft. **32**, 347-350.

Pisecky J. (1986). Standards, specifications and test methods for dry milk powders. In: Concentration and Drying of Foods. MacCarthy D (ed.). Elsevier. pp. 203-220.

Sloth Hansen P. (1980). Production of agglomerated fat-filled milk powder. J. Soc. Dairy Technol. **33**, 19-23.

Swern D. (ed.). (1964). Bailey´s Industrial Oil and Fat Products. 3rd Ed., Interscience Publishers. 117.

Tornberg E, Olsson A, Persson K. (1990). The structural and interfacial properties of food proteins in relation to their function in emulsions. In: Food emulsions. Larsson K, Friberg SE (eds.). Marcel Dekker, New York, 247-326.

Discussion with Reviewers

W.G. Sloof: Is it possible that partial desorption of surface fat on the food powders occurs in the ultra high vacuum during the ESCA measurements?
Authors: From the table of values of the vapor pressures for different triglycerides at different temperatures (Swern, 1964), the boiling temperature for the different triglycerides at 10^{-8} torr can by estimated by extrapolation:

Triglyceride	Desorption temperature at 10^{-8} torr
Tristearin	123°C
Tripalmitin	113°C
Trimyristin	98°C
Trilaurin	77°C
Tricaprin	55°C

The ESCA-measurements are made at room temperature, where according to our calculations, no desorption of the fat will occur.

This is further confirmed with the fact that no particulate degassing is observed when samples of pure fat are exposed to the ultra high vacuum.

W.G. Sloof: Is a contribution of surface contamination to the C and O signals in the ESCA-measurements negligible in the analysis of the food powders as performed?
Authors: The atomic composition estimated by ESCA and the theoretical calculated composition for the pure components corresponds well. This leads us to believe that the surface contamination can be neglected in this case.

W.G. Sloof: Are alternative methods as factor analysis, which also takes chemical shift into account (cf. Briggs and Seah, 1990), considered to deconvolute the measured spectra into the different components?
Authors: The C 1s-peak originating from fat, protein and carbohydrate will have different appearances due to chemical shifts. Using factor analysis is an interesting possibility to increase the power of the method. However, it will be more sensitive to charging and to incorrect charge neutralization of the samples, which will cause shift in the peaks.

V.E. Colombo: Could you explain, in more detail, what you expect from heating of preemulsions?
Authors: From representatives of milk powder manufacturing industry, we know that heat-treatment is one way used to control the hydrophobic properties of milk powders, for instance to get milk powders suitable for the chocolate industry. This is probably due to denaturation of whey protein. We have used bovine serum albumin as a model for whey protein, to investigate the effect of heat-treatment of the protein on the fat encapsulation.

V.E. Colombo: Could you comment, according to your expertise, about a possible relation between the particle size and the porosity of spray-dried whole milk powders on the one side, and the free fat on the other side?
Authors: We have not done any investigation about this relation. Dr. Buma performed an extensive study of the relation between free fat and particle size (Buma, 1971c), and free fat and porosity (Buma, 1971f).

D.A. Driedonks: The results are based on the assumption that the thickness of the surface layer $t >> \lambda$. This assumption seems rather crucial, and is, according to your paper supported by EM-results from Buchheim (1982). Film thicknesses derived from free fat and surface fat data presented in your paper can roughly be estimated to be in the order of 4λ for smaller particles (few μm). This raises the question: how convincing electron micrographs are in estimating film thicknesses. Is the absence of such films based on physical reality, or can it be a consequence of technical limitations of the method.

Authors: Electron microscopy can be used to determine the presence of thin films of crystallin fat (Buchheim, 1982). The fat is distinguished by its crystallinity and it includes several crystal layers, each about 5 nm thick. Very thin films with non-crystalline fat will be hard to distinguish with electron microscopy. The presence of a very thin film of fat will make the underlying protein layer contribute to the ESCA-signal. Fig. 2 shows the depth of information for the ESCA-measurements. Fig. 2 shows that the main part of the ESCA-signal will originate from the outer surface of the first and second lipid layer, making the contribution of the underlying protein layer to the signal small.

D.A. Driedonks: In Figure 7 you show a relation between surface coverage and melting temperature of the fat. You explain the differences in surface coverage by the phase difference of the fat (molten or crystalline) in the spray drier. The particle temperature, however, is determined by the wet bulb temperature rather than the outlet temperature. Taking this into account, does your conclusion on phase differences still hold? How do you explain Sloth Hansen´s results, which seem to be in contradiction with your results?

Authors: The wet bulb temperature determines the droplet temperature before the drying is finalized. The temperature of the dried powder collected in the cyclone will increase until it reaches the outlet temperature particularly in a small sized laboratory spray-dryer. Sloth Hansen (1980) report that the use of low melting fat causes a higher content of free fat than when using fats melting at higher temperatures, which is consistent with our results. On the other hand, Sloth Hansen showed that the wettability could be considerable improved by using a low-melting fat, but the flowability will be deteriorated. A large coverage of low melting fat is expected to reduce flowability. The wettability, measured as dispersability, is strongly depending on the degree of agglomeration. An increased fat coverage might increase the agglomeration, and thereby, reduce the formation of lumps.