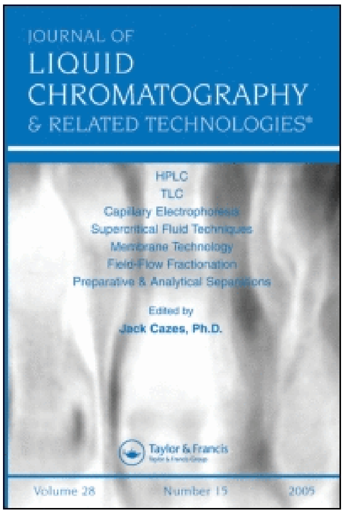

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

STUDY OF THE INFLUENCE OF IONIC STRENGTH AND pH OF THE SUSPENDING MEDIUM ON THE SIZE OF WHEAT STARCH GRANULES, MEASURED BY SEDIMENTATION/STERIC FIELD-FLOW FRACTIONATION

Lambros Farmakis[a]; Athanasia Koliadima[a]; George Karaiskakis[a]
[a] Department of Chemistry, University of Patras, Patras, Greece

To cite this Article Farmakis, Lambros , Koliadima, Athanasia and Karaiskakis, George(2002) 'STUDY OF THE INFLUENCE OF IONIC STRENGTH AND pH OF THE SUSPENDING MEDIUM ON THE SIZE OF WHEAT STARCH GRANULES, MEASURED BY SEDIMENTATION/STERIC FIELD-FLOW FRACTIONATION', Journal of Liquid Chromatography & Related Technologies, 25: 2, 167 — 183

To link to this Article: DOI: 10.1081/JLC-100108738

URL: http://dx.doi.org/10.1081/JLC-100108738

J. LIQ. CHROM. & REL. TECHNOL., 25(2), 167–183 (2002)

STUDY OF THE INFLUENCE OF IONIC STRENGTH AND pH OF THE SUSPENDING MEDIUM ON THE SIZE OF WHEAT STARCH GRANULES, MEASURED BY SEDIMENTATION/STERIC FIELD-FLOW FRACTIONATION

Lambros Farmakis, Athanasia Koliadima,
and George Karaiskakis*

Department of Chemistry, University of Patras,
26500 Patras, Greece

ABSTRACT

The sedimentation/steric field-flow fractionation (Sd/StFFF) technique has been approved as a simple and accurate method for the size separation and characterization of starch granules. In the present work, we further investigate this application by studying the influence of the ionic strength and the pH of the suspending medium on the size of the wheat starch granules measured by Sd/StFFF.

A bimodal size distribution curve was found by Sd/StFFF for the starch granules, in accordance with the results obtained by scanning electron microscopy (SEM). The number and weight average diameters for the large (A-type) and small (B-type)

---

*Corresponding author. E-mail: g.karaiskakis@chemistry.upatras.gr

starch granules are independent of the presence of the indifferent electrolyte KNO_3 in the suspending medium, indicating that disintegration or aggregation phenomena of the starch particles are absent. The later was also verified by SEM. The fact that the suspension pH does not influence the number and weight average diameters of the starch granules is discussed, in relation to the zeta potentials of the particles, which were measured by a microelectrophoresis apparatus.

INTRODUCTION

Starch granules are made up of amylose and/or amylopectin molecules arranged radially. They contain both crystalline and noncrystalline regions in alternating layers. Starch is widely distributed in various plant organs as a storage carbohydrate. As an ingredient of many foods, it is also the most important carbohydrate source in human nutrition. In addition, starch and its derivatives are important industrially, for example, in the paper and textile industries (1,2). Starches of various origin have individual characteristic properties which go back to the shape, size distribution, composition, and crystallinity of the granules.

Much work has been carried out on the influence of the various properties of starch, among which the size of the starch granules on the structure of the final product (3,4). Taking also into account that the large granules are more susceptible to chemical and enzymatic hydrolysis than the small ones, it is of great importance to know the granule size distribution, so as to select the optimal cereal strain to optimize the economy in food industry, because the size and shape of starch granules have been used to determine their botanical origin.

Many methods of particle-size analysis of starch are available, and it is important to realize that different methods may give different results, depending on the complexity of the mixture of particles, such as their shape, porosity, and size distribution (5–7). For polydisperse samples in which the particles are of different sizes, such as the starch sample used in the present work, the description of the particle size can be done by using average diameters (e.g., number and weight average diameter) or size distribution curves (e.g., a histogram or a smooth curve or a cumulative distribution curve). Several techniques are used for the size characterization of starch granules, e.g., light and scanning electron microscopy, coulter counter method, and sedimentation/steric field-flow fractionation. It is the purpose of this work to use the sedimentation/steric field-flow fractionation technique for the study of the influence of the ionic strength and the pH of the suspending medium on the size of the wheat starch granules measured by Sd/StFFF. The suspension ionic strength and pH, influence the wetting and dispersion properties of starch which are dependent on the forces between the surface of the starch and the molecules of the media, compared with forces preventing the adherence of granules to each other, which lead to starch's granule aggregation (8,9).

Field-flow fractionation (FFF) is a one phase-chromatographic system in which an external field or gradient replaces the stationary phase (6,7,10,11). The applied field can be of any type that interacts with the sample components and causes them to move perpendicular to the flow direction in the open channel. The most highly developed of the various FFF modes is sedimentation FFF (SdFFF), in which the separation of suspended particles is performed with a single, continuously flowing mobile phase in a very thin, open channel under the influence of an external centrifugal force field (11–13).

In SdFFF the retention volume V_{ri} is related to spherical particle diameter (or equivalent spherical particle diameter for nonspheres), d_i, by the expression (12,13):

$$V_{\mathrm{ri}} = \frac{\pi G w \Delta\rho V^{\mathrm{o}}}{36kT} d_i^3 \tag{1}$$

where V^{o} is the volume and w the thickness of the FFF channel, k is the Boltzmann constant, T is temperature, G is centrifugal acceleration, and $\Delta\rho$ is the density difference between the particle and the carrier solution. It is known, (12) that with the aid of Equation (1), a particle-diameter scale can be grafted to the fractogram along the time or elution volume axis.

In steric FFF (StFFF) the retention volume V_{ri} is related to the diameter d_i via the expression (14,15):

$$V_{\mathrm{ri}} = \frac{wV^{\mathrm{o}}}{3\gamma} \cdot \frac{1}{d_i} \tag{2}$$

where γ is called the steric correction factor and accounts for the drag-induced reduction in the particle velocity. Parameter γ depends, among other parameters, on flow velocity, particle diameter, and relative shape. So, in order to get particle diameters in sedimentation/steric FFF (Sd/StFFF), where the applied field is generated by a centrifuge, a calibration curve is needed. It has been shown previously (6) that a plot of $\log t_{\mathrm{ri}}$ vs. $\log d_i$ (where t_{ri} is the retention time) is approximately linear over a wide diameter range for standard polystyrene latex spheres. When sample particles have a density different from that of standard particles used, as it is the case here, the calibration curve for the standards can be utilized, providing the product $G\Delta\rho$ must be the same for the starch granules and the latex (6).

EXPERIMENTAL

The experimental procedure has been described in detail elsewhere (7). In all experiments, the sedimentation FFF system employed had a channel void volume of 1.57 cm^3. The outside wall of the channel was bare, polished Hastelloy C alloy, which is principally Ni (56%) with 15% Cr, 17% Mo, 5% Fe, 4% W, and traces of Mn and Si. The radius of rotation was 6.85 cm. The analysis was performed with a Gilson Minipuls 2 peristaltic pump coupled with a Gilson model 111 Holochrome UV detector operated at 254 nm, and a Linseis model L6522 recorder.

Triply distilled, CO_2-free water, containing 0.5% by volume of low foaming, low alkalinity, phosphate, chromate, and silicate-free detergent FL-70 (Fisher Scientific Co.) and 0.02% w/w NaN_3 (Fluka), has been employed as carrier. The manufacturer supplying FL-70 advises that this is an uncharacterized mix of anionic and nonionic surfactants and, also, that a 2% solution of FL-70 gives a pH of 10.5.

The electrolyte added to the carrier solution to adjust its ionic strength was potassium nitrate (KNO_3) from Riedel-De Haen A.G., while the pH of starch dispersion was adjusted with HNO_3 (from Riedel-De Haen A.G.) and KOH (from Merck A.G.).

Standard polystyrene latex spheres from Polysciences, Inc., with nominal diameters of 5.725 ± 0.278, 10.568 ± 1.034, 14.571 ± 1.657, 22.000 ± 2.593, and 25.962 ± 2.718 μm were used for the calibration plot.

Starch from wheat samples (Catalog No. 85647, Fluka) was employed. The starch granules were suspended in the carrier liquid and sonicated for 5 min as a further aid to particle dispersion. The concentration of the resulting starch granule suspension was kept constant (10 mg/mL) in all experiments. Injection of 100 μL volume of the starch suspension was made into the channel by a microsyringe. Following injection, the longitudinal flow ($= 195\,mL\,h^{-1}$) was stopped for 10 min to allow for sample relaxation.

According to the principle of density compensation described earlier (6,16), and taking into account that the densities of the starch and the polystyrene latexes are 1.51 g/mL and 1.05 g/mL (6), respectively, the field strength G for starch must be reduced by a factor of 10.3 compared to that used with polystyrene latex spheres for the calibration plot. Since G for latexes was $G = 169\,g = 1000$ rpm, the appropriate field strength for starch used was $G = 16.4\,g = 312$ rpm.

The electrophoretic mobility and the zeta (ζ) potential of dispersed starch samples were measured by using the Zetasizer 5000 equipment from Malvern, while the pH of starch dispersion, which was adjusted with HNO_3 or KOH, was measured by the pH-meter model 507 from CRISON (Spain).

For comparison purposes, scanning electron micrographs of the wheat starch granules dispersed in different media were obtained by using a JEOL JSM-5200 scanning electron microscope (SEM) from JEOL (Tokyo, Japan).

RESULTS AND DISCUSSION

Figure 1 is a “raw” fractogram, which expresses the detector response profile over the separation retention volume span for the wheat starch sample. It shows a bimodal size distribution for the populations of A-large and B-small wheat starch granules, which is more acceptable in literature (8,17,18). Although, it must be pointed out that various basic books dealing with starch (2,19), refer also to the

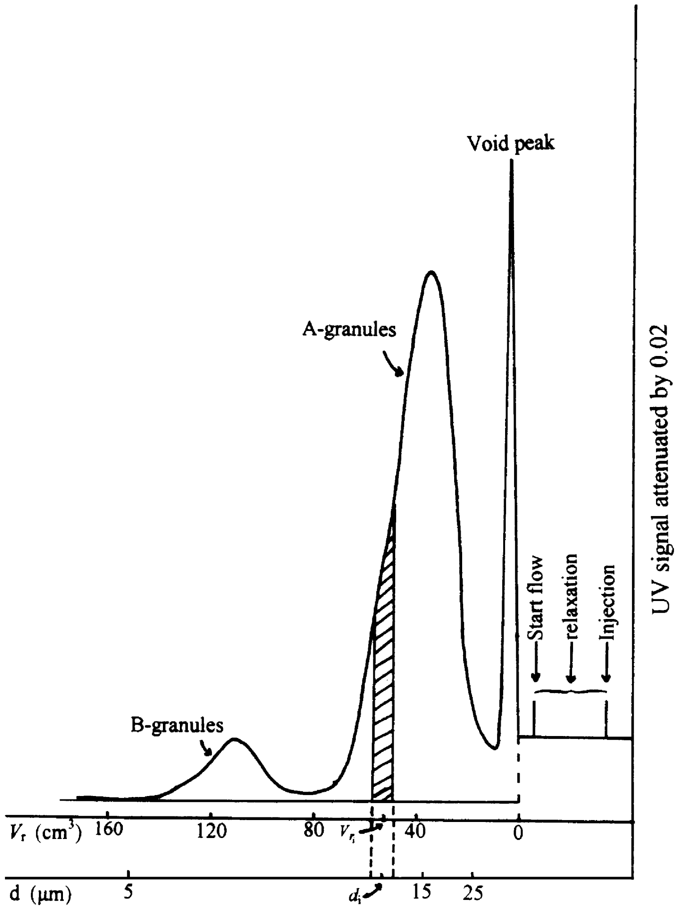

Figure 1. Fractogram and particle diameter scale of wheat starch granules obtained by Sd/StFFF, showing a bimodal size distribution. Centrifugal field = 312 RPM; flow = 195 cm^3 h^{-1}; sample = 100 µL; carrier solution: 0.5% v/v FL-70 + 0.02% w/w $NaN_3 + 3 \cdot 10^{-2}$ M KNO_3.

possibility of a trimodal size distribution for wheat starch granules. The desired particle-size distribution curve, which is a plot of true particle concentration as a function of particle diameter, was found as follows (6,7,14,20,21):

The elution curve (see Fig. 1) is divided into between ten and fifteen areas wherein particle diameter, d_i, which corresponds to the retention volume V_{ri}, is considered constant over the interval and represented by the midpoint of it. The division process is performed for each starch peak in the bimodal fractogram by using the "perpendicular drop method," (22) not including the void peak. The d_i values are determined by using the density compensation methodology described previously (6). The used calibration plot (cf. Fig. 2) obeys the relationship:

$$\log t_{\mathrm{ri}} = -1.3397 \log d_i + 2.6196 \tag{3}$$

From all the d_{i} values of a fractogram, the weight average particle diameter, d_w, is determined using an appropriate computer program, by the expression (7):

$$d_w = \frac{\sum_i d_i^4 N_i}{\sum_i d_i^3 N_i} = \frac{\sum_i d_i w_i}{\sum_i w_i} = \frac{\sum_i d_i w_i}{W} \tag{4}$$

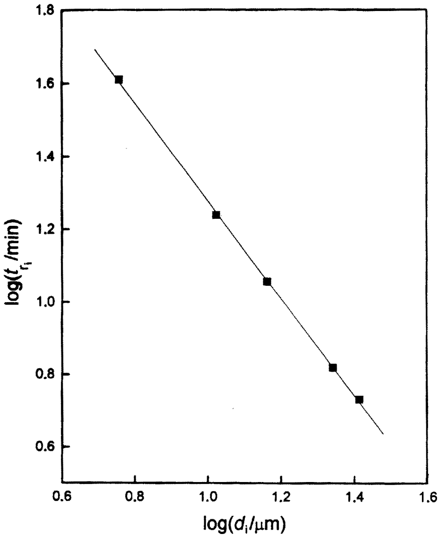

Figure 2. Calibration plot of log(t_{ri}/min) vs. log (d_i/μm) obtained by Sd/StFFF by using standard polystyrene latex spheres. Centrifugal field = 1000 RPM; flow = 195 cm^3 h^{-1}; sample = 100 μL; carrier solution: 0.5% v/v FL-70 + 0.02% w/w NaN$_3$.

where N_i is the number of the particles having constant diameter d_i, w_i is the weight of the N_i particles, which is proportional to the area of the shaded section in the fractogram (see Fig. 1), and W is the weight of the whole number of eluted particles N, which is proportional to the total area under the eluted curve. We use the hypothesis that the weight of some particles is proportional to the corresponding area of the fractogram, even it is not correct, as we are mainly interested in the variation of the number and weight average diameters of the barley starch granules with the ionic strength and the pH of the suspending medium, and not in the determination of their absolute values. In addition, due to the high polydispersity of the barley starch granules, the correction of the number and weight average particle diameters due to the above hypothesis should be meaningless.

The standard deviation, σ_{d_w}, of the weight average particle diameter was calculated from the known relation:

$$\sigma_{d_w} = \left[\frac{\sum_i (d_i - d_w)^2 w_i}{\sum_i w_i} \right]^{1/2} \tag{5}$$

The number average particle diameter, d_N, was calculated by using the relation (7):

$$d_N = \frac{\sum_i d_i N_i}{\sum_i N_i} = \frac{\sum_i \frac{w_i}{d_i^2}}{\sum_i \frac{w_i}{d_i^3}} \tag{6}$$

The standard deviation, σ_{d_N}, of the number average particle diameter was found from the expression:

$$\sigma_{d_N} = \left[\frac{\sum_i (d_i - d_N)^2 N_i}{\sum_i N_i - 1} \right]^{1/2} \tag{7}$$

Apart from the d_w and d_N values determined from Equations (4) and (6), respectively, there are two other ways of presenting a description of a polydisperse system such as the wheat starch sample, in terms of the d_i values in each fractogram calculated by the methodology described previously (6).

A common graphical representation of a frequency distribution is the histogram (or in the form of a smooth curve), a bar graph in which the diameters d_i are plotted as the abscissa and the height of the bar is proportional to the number of particles with constant particle diameter d_i. The latter is proportional to the area of the shaded section in the fractogram (see Fig. 1), only in the case when the size of the particles is kept constant. The ordinate is defined as the fraction of particles, n_i, with constant diameter d_i, eluted in the shaded section of the fractogram, which is proportional to the fraction of area of this shaded section, f_i. In Figs. 3a and 3b are given the histograms, in the form of smooth curves, obtained from Sd/StFFF and SEM, respectively, for the wheat starch sample.

These kinds of data can also be represented as a cumulative curve in which the fraction of particles, $n_{T,i}$ (or the corresponding fraction of area, $f_{T,i}$) having diameters less than, and including a particular diameter d_i, are plotted vs. d_i. Figs. 4a and 4b show the cumulative plots for the same data shown in Figs. 3a and 3b, respectively.

The fractograms obtained by Sd/StFFF for the wheat starch granules dispersed in various media containing different amounts of the electrolyte KNO_3, with the corresponding SEM pictures of the dry suspensions, are shown in Fig. 5. As can be seen, in all cases, both the fractograms and the SEM pictures have the same form, showing that aggregation or disintegration phenomena of the wheat starch granules are absent; even the concentration of the electrolyte KNO_3 in the suspending medium varies by a factor of 100. For the verification of the above observation, the influence of the suspension ionic strength on the measured Sd/StFFF number (d_N) and weight- (d_w) average diameters of the wheat starch granules was studied.

The variation of the number and the weight average diameters of the wheat starch granules with the concentration of the indifferent electrolyte KNO_3 at constant surfactant concentration (0.5% v/v FL-70), together with the corresponding pH values are compiled in Tables 1 and 2. Moreover, in Tables 1 and 2 are given the number, d_N^*, and weight, d_w^*, average diameters of about 300 starch granules (approximately 150 granules from each population) obtained from SEM with the corresponding standard deviations for the two populations of the wheat starch granules. Taking into consideration the relatively big standard deviations of the average values of the diameters determined by Sd/StFFF, due to the polydispersity of each starch population, as well as the fact that the preparation procedure in SEM brings the granules to the dry state from the wet one used in Sd/StFFF, the agreement between the average diameters of the starch granules determined by Sd/StFFF and those found by SEM, is relatively satisfactory.

The difference between the average particle diameters found by Sd/StFFF and those obtained by SEM can be also attributed to the fact that all subtechniques of FFF give weight average particle diameters, since the detector response is a function of particle concentration, as well as of particle size, while SEM gives number average particle diameters. For spherical monodisperse particles, these two diameters are identical, but for our case, in which the starch granules of each population are nearly spherical but polydisperse, they are different. The bigger the difference between these two average

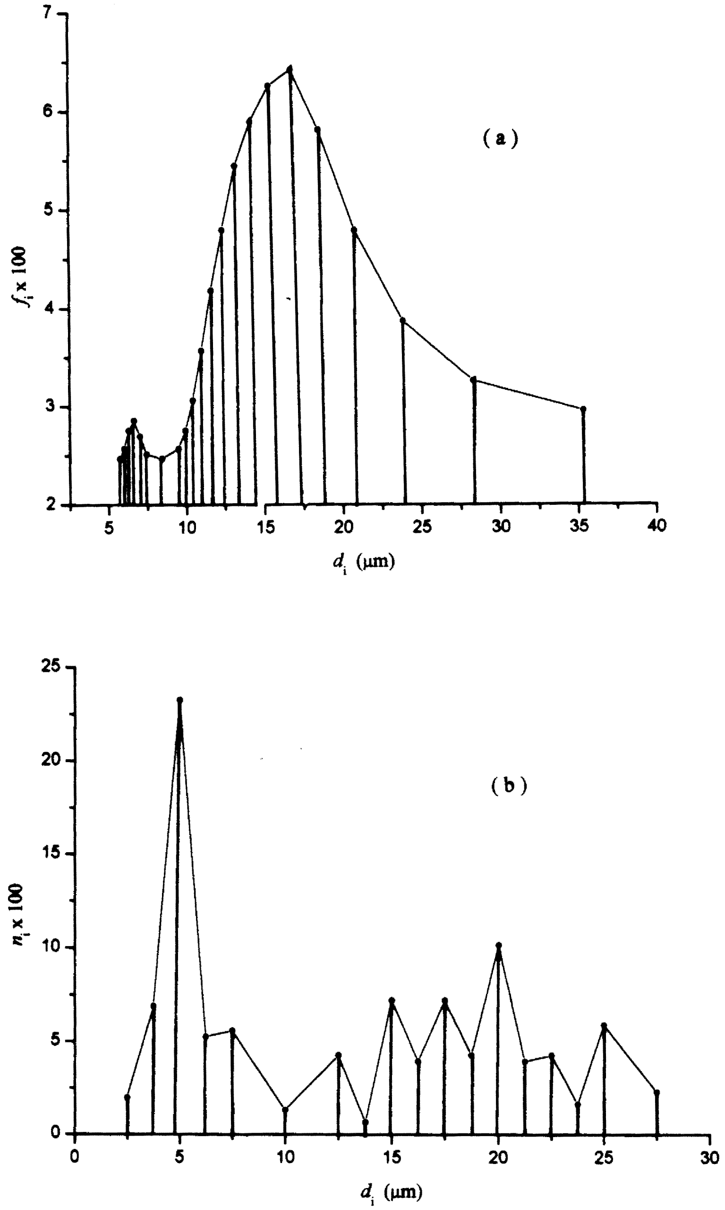

Figure 3. Graphical representation as a histogram of the diameters for the wheat starch granules obtained (a) by Sd/StFFF (carrier solution = 0.5% v/v FL-70 + 0.02% w/w $NaN_3 + 3 \cdot 10^{-2}$ M KNO_3), and (b) by scanning electron microscopy (SEM).

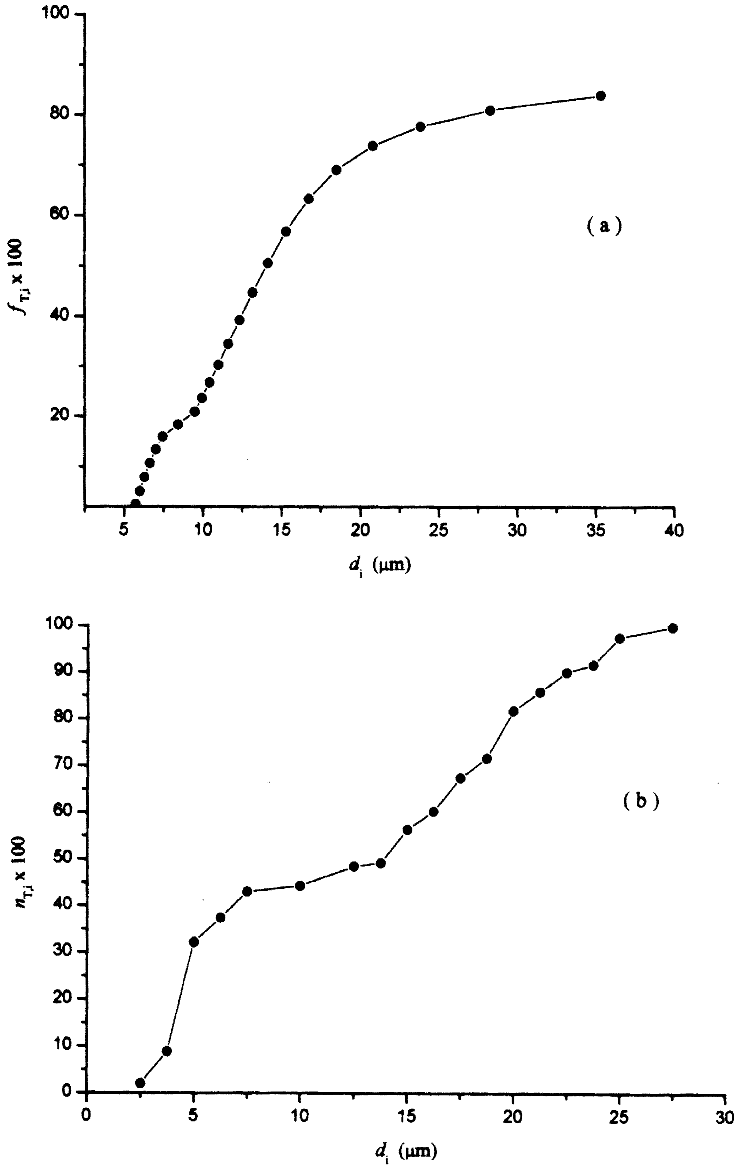

Figure 4. Cumulative distribution curves of the diameters for the wheat starch granules obtained (a) by Sd/StFFF (the experimental conditions are the same as those of Figure 3a), and (b) by SEM.

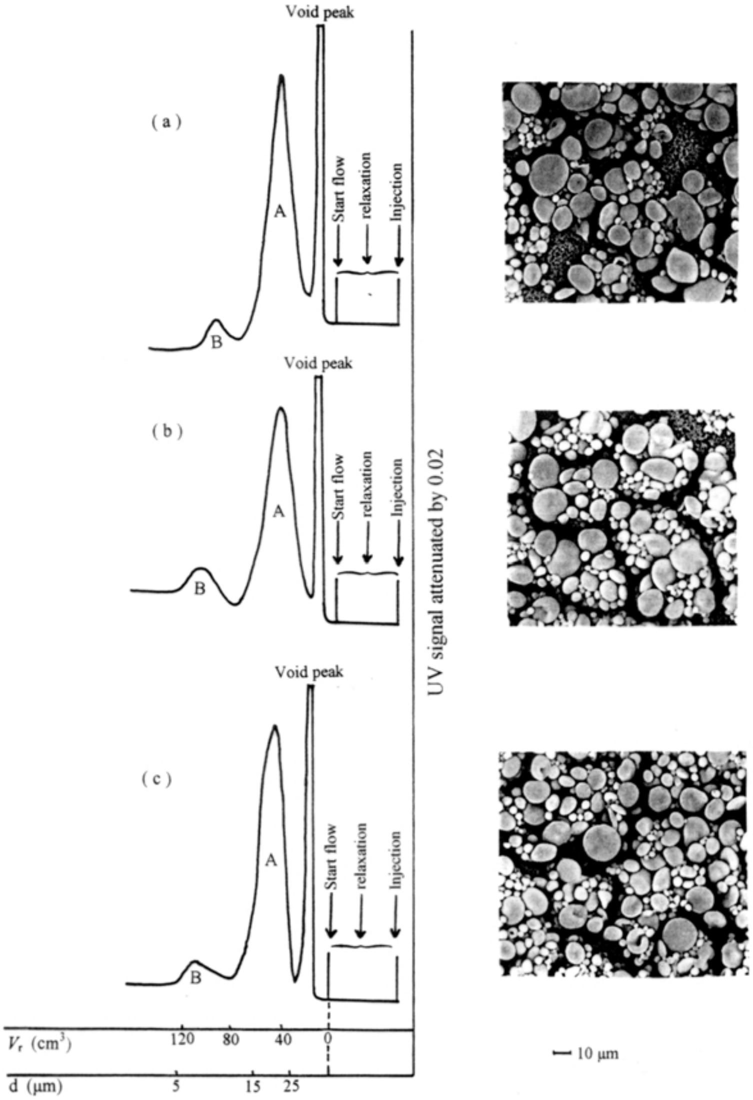

Figure 5. Fractograms of the wheat starch granules obtained by Sd/StFFF at various ionic strengths of the suspending medium, with the corresponding SEM pictures of the dry suspensions: (a) $c_{\mathrm{KNO_3}} = 10^{-3}$ M; (b) $c_{\mathrm{KNO_3}} = 10^{-2}$ M; (c) $c_{\mathrm{KNO_3}} = 10^{-1}$ M.

Table 1. Number Average Diameters, d_N, with Their Standard Deviations, σ_{d_N}, for the Large and Small Wheat Starch Granules*

		$d_N \pm \sigma_{d_N}$ (μ)		$d_N^* \pm \sigma_{d_N^*}$ (μ)	
Carrier Solution	pH	Large	Small	Large	Small
0.5%FL-70 + 0% KNO_3	9.7	12.6 ± 3.3	6.5 ± 0.6	18.0 ± 5.1	4.8 ± 0.9
0.5%FL-70 + 1×10^{-3} M KNO_3	9.7	12.5 ± 3.3	6.8 ± 0.6		
0.5%FL-70 + 3×10^{-3} M KNO_3	9.8	12.6 ± 3.2	6.7 ± 0.6		
0.5%FL-70 + 7×10^{-3} M KNO_3	9.6	12.7 ± 3.2	6.5 ± 0.6		
0.5%FL-70 + 1×10^{-2} M KNO_3	9.7	11.6 ± 2.9	6.4 ± 0.6		
0.5%FL-70 + 3×10^{-2} M KNO_3	9.8	12.5 ± 3.4	6.4 ± 0.6		
0.5%FL-70 + 7×10^{-2} M KNO_3	9.7	12.7 ± 3.5	7.0 ± 0.7		
0.5%FL-70 + 1×10^{-1} M KNO_3	9.7	13.6 ± 3.0	6.8 ± 0.6		

*Determined by the Sd/StFFF technique at various potassium nitrate (KNO_3) concentrations of the suspending medium, as well as number average diameter, d_N^*, with its standard deviation, $\sigma_{d_N^*}$, for the same sample obtained by SEM.

Table 2. Weight Average Diameters, d_w, with Their Standard Deviations, σ_{d_w}, for the Large and Small Wheat Starch Granules*

		$d_w \pm \sigma_{d_w}$ (μ)		$d_w^* \pm \sigma_{d_w^*}$ (μ)	
Carrier Solution	pH	Large	Small	Large	Small
0.5%FL-70 + 0% KNO_3	9.7	16.3 ± 5.1	6.7 ± 0.6	21.4 ± 3.9	5.2 ± 0.7
0.5%FL-70 + 1×10^{-3} M KNO_3	9.7	16.3 ± 6.1	6.9 ± 0.6		
0.5%FL-70 + 3×10^{-3} M KNO_3	9.8	16.0 ± 5.7	6.9 ± 0.6		
0.5%FL-70 + 7×10^{-3} M KNO_3	9.6	15.8 ± 4.7	6.7 ± 1.0		
0.5%FL-70 + 1×10^{-2} M KNO_3	9.7	14.6 ± 4.8	6.6 ± 0.7		
0.5%FL-70 + 3×10^{-2} M KNO_3	9.8	16.9 ± 7.1	6.5 ± 0.6		
0.5%FL-70 + 7×10^{-2} M KNO_3	9.7	16.9 ± 6.4	7.2 ± 0.7		
0.5%FL-70 + 1×10^{-1} M KNO_3	9.7	15.9 ± 4.1	6.9 ± 0.7		

*Determined by the Sd/StFFF technique at various potassium nitrate (KNO_3) concentrations of the suspending medium, as well as weight average diameter, d_w^*, with its standard deviation, $\sigma_{d_w^*}$, for the same sample obtained by SEM.

diameters, the larger the polydispersity of the starch granules for that particular population. Thus, the comparison between these two diameters is an approximation.

A statistical analysis of the various d_N and d_w values obtained by Sd/StFFF at various ionic strengths of the suspending medium, taking into account their standard deviations σ_{d_N} and σ_{d_w}, respectively, indicates that all these values do not differ significantly from each other. This observation leads to the conclusion that the wheat starch sample, in the presence of relatively large quantities of the indifferent electrolyte KNO_3 in the suspending medium, is stable and neither disintegration nor aggregation processes take place. The SEM pictures of Fig. 5 also exclude both processes. The difference between the number and weight average diameters means that, although there is a great number of small starch granules, the larger starch granules contribute more to the mass of the starch.

The obtained Sd/StFFF fractograms for the wheat starch sample dispersed in various media, which have different pH values with the corresponding SEM pictures of the dry suspensions, are shown in Figure 6. The latter indicate that the form of the fractograms and of the SEM pictures are independent of the suspension pH, showing that disintegration or aggregation phenomena of the wheat starch granules are absent. For the confirmation of this observation, the variation of the number and weight average diameters of the wheat starch granules measured by Sd/StFFF with the pH of the suspending medium was studied. The dependence of number and weight average diameters of starch granules on the suspension pH, at constant ionic strength (7.0×10^{-2}), is shown in Tables 3 and 4. It can be seen that the suspension pH does not influence the number and weight average diameters of the two populations of the wheat starch granules in the pH range 7–11, in which no adhesion of the starch particles occurs at the beginning of the SdFFF channel wall. The latter is also verified by the SEM pictures of Fig. 6. Figure 7 shows the zeta potentials of the wheat starch granules as a function of the suspension pH and at constant ionic strength (5.4×10^{-2}). The zeta potential-pH profile of wheat starch granules is consistent with the presence of both positively and negatively charged groups at the surface, due to the fact that wheat starch granules carry both lipids and protein at their surfaces. The negative zeta potentials in the pH range 2.5–12.0 confirm the "anionic behaviour" of starch. It is obvious that the isoelectric point (i.e.p.), $pH_{i.e.p.} \approx 2.5$, is out of the working pH range. As it may be seen, the influence of $[H^+]$ concentration in solution on the zeta potential of starch granules is not dramatic in the pH range $7.0 < pH < 11.0$. The sharp increase of the zeta potentials at $pH < 7$, a value which is out of the working range, may be due to increased solubility of the wheat starch granules.

In all cases of Tables 3 and 4, in which elution peaks were obtained, pH ranged between 7.0 and 11.0, and since H^+ are not potential determining ions, it is not expected that such a change in pH would markedly influence the electrophoretic mobility and the zeta potential measured.

It is noteworthy, that the Hastelloy C channel wall, which is a type of stainless steel, below approximately pH 6 is positively charged, while at $pH > 6$ it is negatively charged (23). Therefore, under our experimental conditions summarized

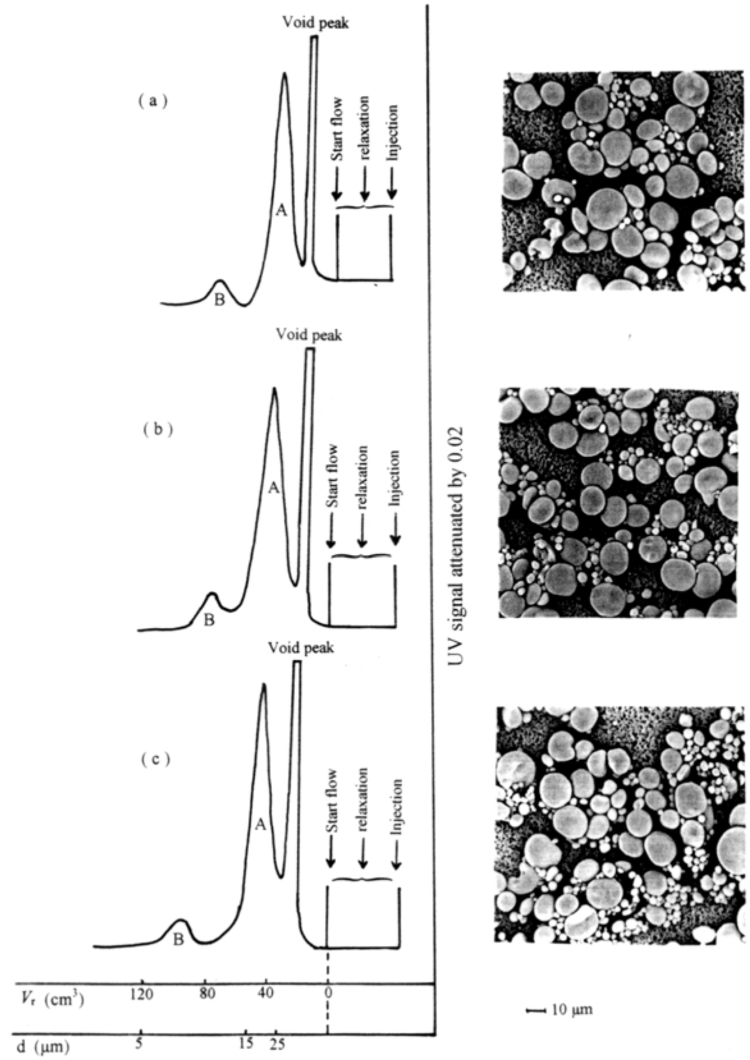

Figure 6. Fractograms of the wheat starch granules obtained by Sd/StFFF at various pH values of the suspending medium, with the corresponding SEM pictures of the dry suspensions: (a) pH = 8.0; (b) pH = 9.0; (c) pH = 10.0.

in Tables 3 and 4, in which the wheat starch granules were characterized by Sd/StFFF, the stainless steel channel wall is negatively charged, thus making the possibility of adhesion or interaction of the wheat starch granules – which are also negatively charged in that particular pH range with the SdFFF column very unlikely.

Table 3. Number Average Diameters, d_N, with Their Standard Deviations, σ_{d_N}, for the Large and Small Wheat Starch Granules*

	$d_N \pm \sigma_{d_N}$ (μ)	
pH	Large	Small
3.7	–	–
5.0	–	–
7.0	12.6 ± 3.4	6.5 ± 0.5
8.0	13.3 ± 3.2	6.2 ± 0.6
9.0	12.8 ± 3.6	6.0 ± 0.8
10.0	12.7 ± 3.8	5.8 ± 0.8
11.0	12.7 ± 3.7	6.6 ± 0.7

*Determined by the Sd/StFFF technique at various pH values of the suspending medium.

Table 4. Weight Average Diameters, d_w, with Their Standard Deviations, σ_{d_w}, for the Large and Small Wheat Starch Granules*

	$d_w \pm \sigma_{d_w}$ (μ)	
pH	Large	Small
3.7	–	–
5.0	–	–
7.0	16.4 ± 5.8	6.7 ± 0.6
8.0	16.2 ± 4.5	6.2 ± 0.7
9.0	15.7 ± 4.7	6.3 ± 0.9
10.0	16.8 ± 6.1	5.9 ± 1.0
11.0	16.5 ± 5.7	6.8 ± 0.9

*Obtained by Sd/StFFF at various pH values of the suspending medium.

Interactions, however, between the starch granules are of importance in the steric range, corresponding to the conditions of the present work.

Since the surface of the Hastelloy C column is positively charged in the first two cases of Tables 3 and 4 (23), and the starch particles have opposite charges, adhesion takes place, the extent of which, is larger in the lower pH case where the column is more positive. This was experimentally verified by the Sd/StFFF

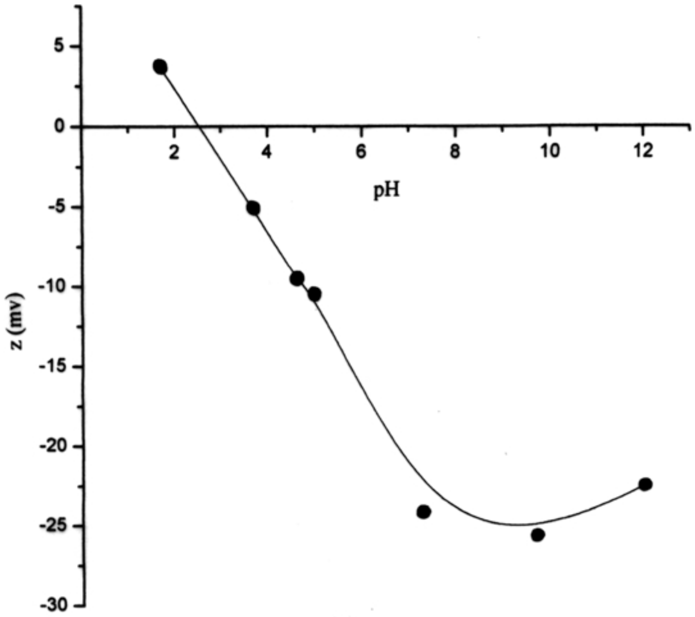

Figure 7. Zeta (z) potential of wheat starch granules as a function of the suspension pH. Carrier solution: 0.5% v/v FL-70 + 0.02 w/w NaN_3 + HNO_3 (or KOH).

technique, in which no elution curve was obtained following the injection of the wheat starch granules into the FFF channel (cf. the first two cases in Tables 3 and 4).

As a general conclusion, one could say that the suspension pH and ionic strength do not influence the number and weight average diameters of the wheat starch granules measured by the sedimentation/steric field-flow fractionation technique, showing that aggregation and disintegration phenomena are absent.

ACKNOWLEDGMENTS

The authors would like to pay tribute to the services of the late Professor J.C. Giddings, who supplied the SdFFF system. This work was financially supported by the European Commision Contract No. ERB IC15-CT98-0909.

REFERENCES

1. Belitz, H.D.; Grosch, W. *Food Chemistry*, Translation from the Fourth German Ed.; Burghagen, M.M., Hadziyev, D., Hessel, P., Jordan, S., Sprinz, C., Eds.; Springer: Berlin, 1999.

2. BeMiller, J.N.; Whistler, R.L. *Food Chemistry*, Fennema, O.R., Ed.; Marcel Dekker: New York, 1996.
3. *Industrial Uses of Starch and its Derivatives*, Radley, J.A., Ed.; Applied Science Publishers Ltd.: London, 1976.
4. Kent-Jones, D.W.; Mitchell, E.F. *The Practice and Science of Bread-Making*, Northern Publ. Co.: Liverpool, 1962.
5. Evers, A.D.; Greenwood, C.T.; Muir, D.D; Venables, C. Starch, **1974**, *26*, 42.
6. Moon, M.H.; Giddings, J.C. J. Food Sci. **1993**, *58*, 1166.
7. Farmakis, L.; Sakellaraki, J.; Koliadima, A.; Gavril, D.; Karaiskakis, G. Starch **2000**, *52*, 275.
8. Marsh, R.A.; Waight, S.G.; Wycombe, H. Starch **1982**, *34*, 149.
9. Hiemenz, P.C.; *Principles of Colloid and Surface Chemistry*, Marcel Dekker: New York, 1977.
10. Giddings, J.C. Anal. Chem. **1981**, *53*, 1170A.
11. Karaiskakis, G.; Myers, M.; Caldwell, K.D.; Giddings, J.C. Anal. Chem. 1981, *53*, 13.
12. Giddings, J.C.; Karaiskakis, G.; Caldwell, K.D.; Myers, M.N. J. Colloid Interf. Sci. **1983**, *92*, 66.
13. Athanasopoulou, A.; Gavril, D.; Koliadima, A.; Karaiskakis, G. J. Chromatogr. A **1999**, *845*, 293.
14. Dalas, E.; Karaiskakis, G. Coll. & Surf. **1987**, *28*, 169.
15. Dalas, E.; Koutsoukos, P.; Karaiskakis, G. Colloid Polym. Sci. 1990, *268*, 155.
16. Giddings, J.C.; Moon, M.H.; Williams, P.S.; Myers, M.N. Anal. Chem. **1991**, *63*, 1366.
17. Jane, J.L.; Kasemsuwan, T.; Leas, S.; Zobel, H.; Robyt, J.F. Starch **1994**, *46*, 121.
18. MacMasters, M.M.; Wolf, M.J.; Seckinger, H.L. Agric. Food Chem. **1957**, *5*, 455.
19. Cornell, H.J.; Hoveling, A.W. *Wheat: Chemistry and Utilization*, Technomic Publishing Co. Inc.: Lancaster (USA), 1998.
20. Yang, F.S.; Caldwell, K.D.; Giddings, J.C. J. Colloid Interf. Sci. **1983**, *92*, 81.
21. Reschiglian, P.; Torsi, G. Chromatographia **1995**, *40*, 467.
22. Leathard, D.A. In *New Developments in Gas Chromatography*, Purnell, H., Ed.; John Wiley & Sons, Inc.: New York, 1973.
23. Thomson, G.; Kallay, N.; Matijevic, E. Chem. Engin. Sci. **1983**, *38*, 1901.

Received July 18, 2001
Accepted August 7, 2001
Manuscript 5622

Downloaded At: 09:11 24 January 2011

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Order now!

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081JLC100108738