Characterization of Ground Grain Products*

*This application note is based on a German article by Julia Schick and Prof. Dr. Klaus Lösche from the ttz Bremerhaven BILB/EIBT in Bremerhaven, Germany. The original article "Charakterisierung von Getreidemahlerzeugnissen durch eine Partikelladungsmessung (PCD: Particle Charge Detector)" was published in the journal Getreidetechnologie, Heft 1 Januar/Februar/März 2010, ISSN 1869-2303

Introduction

The functional properties of ground grain products or foodstuffs in general depend on the characteristics and interactions of their components such as starch, proteins, lipids and salts. On account of their chemical or overall physical attributes, ground cereal products have a significant influence on the resultant techno-functional properties of the foodstuffs concerned. In this context, it appears worthwhile to take a look at the surface charges of raw materials such as ground grain products in order to gain more in-depth information than was accessible in the past. It may be assumed that the specific charges of polyelectrolytes such as proteins or gluten give rise to a spatial structure which, among others, explains their functionality, for instance their rheology. Against this background a specific method has been applied to measure the surface charge of dispersed particles in aqueous systems by using a Mütek PCD Particle Charge Detector (Fig. 1) with a view to identifying and characterising primarily the surface charges of various different ground grain products or other raw materials. The detector is used to measure the mass specific charge as well as the buffer capacity and the isoelectric point for correlation with functional properties of foodstuffs. This approach enables certain interactions of components or additives in foodstuff systems to be identified, recipes to be optimised or processes to be modified in a targeted manner.

Measurements with the Mütek PCD Particle Charge Detector provide a novel method for application in food analytics which opens up altogether new and numerous options to characterize, among others, ground grain products, raw materials, additives or finished products.

Fig. 1: Mütek™ PCD-04 Particle Charge Detector with automatic titrator PCD-T3

Measuring principle

The Mütek PCD Particle Charge Detector measures the total charge of suspended particles in aqueous solutions by inducing a streaming potential. Macromolecules present in an aqueous suspension adsorb at the wall of a test cell made of polytetrafluoroethene (PTFE) where they form an electric double layer. Inside the cell, a PTFE piston oscillates up and down. A narrow gap is provided between cell wall and piston. As the piston oscillates, the suspension medium is moved past the electric double layer so that the ion cloud surrounding the particles is sheared off. As charges are sheared off the double layer, an electric field is built up. As soon as equilibrium is attained, two electrodes arranged at the top and bottom ends of the test cell identify a potential that is called streaming potential. Not only adsorbed but likewise freely scattered particles in the test liquid contribute to the streaming potential as they are also subject to shear stresses although to a lesser extent. Fig. 2 shows schematically a PCD measuring cell with adsorbed charged macromolecules and the oscillating movement of the piston.

The measuring result obtained from the Mütek PCD Particle Charge Detector is the streaming potential. The charge quantity of a sample can be determined by titration with a polyelectrolyte solution of known charge and which is opposite in sign to the sample. The state of charge neutralisation during the titration process is identified by measuring the streaming potential: the point of zero charge is reached when the streaming potential is at 0 mV.

Titration of an anionic sample is effected with Poly-Dadmac (poly-diallyldimethyl ammonium chloride), a cationic polyelectrolyte, whereas cationically charged samples are titrated with an anionic polyelectrolyte Pes-Na (poly-vinylsulfonic acid, sodium salt).

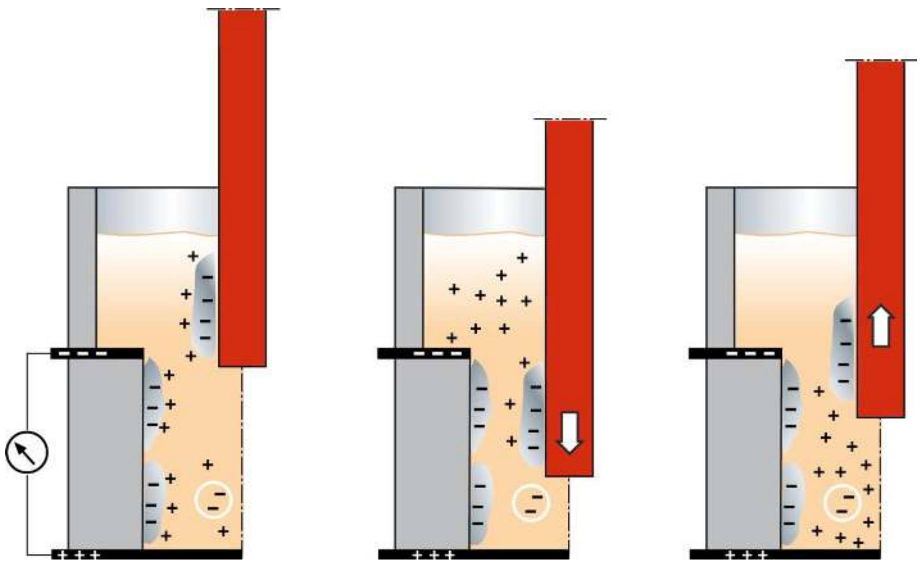

Fig. 2: Schematic of a PCD measuring cell with oscillating piston movement

Addition of a polyelectrolyte with opposite charge triggers a complexation reaction between the polyanion and the polycation, thus leading to symplex formation. In the following, two limit models of symplex formation will be described.

The two limit models are known as ladder model and scrambled-egg model (Fig. 3).

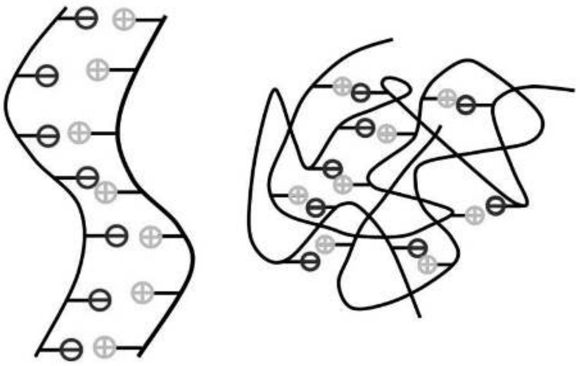

Fig. 3: Symplexing models: (a) ladder model (b) scrambled-egg model

Calculations

Let a 1:1 stoichiometry be assumed for symplex formation. In this case, the total charge q of the tested sample can be calculated by formula 1 from the consumption of polyelectrolyte solution V[l] and the concentration of the polyelectrolyte solution c[mol/l].

Formula 1: Calculation of the total charge q in mol

$$q = V \times c$$

where q = total charge [mol]; V = volume of consumed titrant [l]; c = titrant concentration [mol/l])

Taking the Faraday constant into account, a molar reference can be established according to formula 2.

Formula 2: Calculation of the total charge Q in Coulomb

$$Q = q \times F$$

where Q = total charge [C]; F = Faraday constant = 96.486 C/mol

The mass-specific charge Q_M of the sample is calculated using formula 3.

Formula 3: Calculation of the mass-specific charge Q_M in C/g

$$Q_M = Q / m$$

where Q_M = total charge [C/g]; Q = total charge [C]; m = solids of the sample or of its active substance [g])

Characterization of ground grain products with the Mütek™ PCD

Measurements with the Mütek PCD Particle Charge Detector quickly and easily identify the surface charge of suspended ground grain or cereal products (flour-water suspensions). If the influences of swelling time and swelling temperature on the measured results are taken into acount, highly coincident multiple determinations of surface charges will be obtained so that this test method lends itself, e.g., to the characterisation of functional properties.

To specify an anionic or cationic surface charge of a sample, the charge measuring results are shown preceded by the sign of the measured streaming potential.

If charge titration is applied to various ground grain products, measuring values of the kind shown in the graphic in Fig. 4 will be obtained.

Obviously, the various products can be clearly differentiated by their mass-specific charges. For example, after a swelling time of approx. 20 min., whole grain wheat flour exhibits a charge of approx. -8.5 Coulomb/g as compared to whole grain flour einkorn (triticum monoccum) with a charge of approx. -12 C/g or whole grain flour emmer (triticum dicoccum) with approx. -17 C/g. The whole grain flour kamut (durum wheat, triticum turgidum subsp. polonicum), too, is distinguishable from other types of grain by its charge level (Fig. 4).

Evidently, charges are dependent on the milling yield, since wheat flour type 1050 (harvested 2008) shows altogether different charge levels compared to whole grain products. In the case of wheat flour type 1050, the initial charge compared to whole grain flours is at approx. -5 C/g and thus distinctly less anionic.

It appears it is primarily the bran components of ground grain products which carry anionic charges (celluloses, hemicelluloses, phytates etc.) and which may be distinguished individually for the various types of grains.

When looking at the evolution of the mass-specific charge of a wheat flour type 1050 (kinetics), a sigmoidal run vs. the swelling time at 20°C is detected. In other words, at the onset of the swelling time of an aqueous wheat flour suspension, charge measurements reveal clearly anionic values which, however, undergo electric and dynamic changes along further evolution. In the end, merely faintly anionic charges of approx. -1 C/g are recorded. For other types of wheat flour with a lower extraction rate, charge measurements frequently indicate finite values within the faintly cationic range (cf. Fig. 6). This suggests the occurrence of a charge reversal during development of a dough.

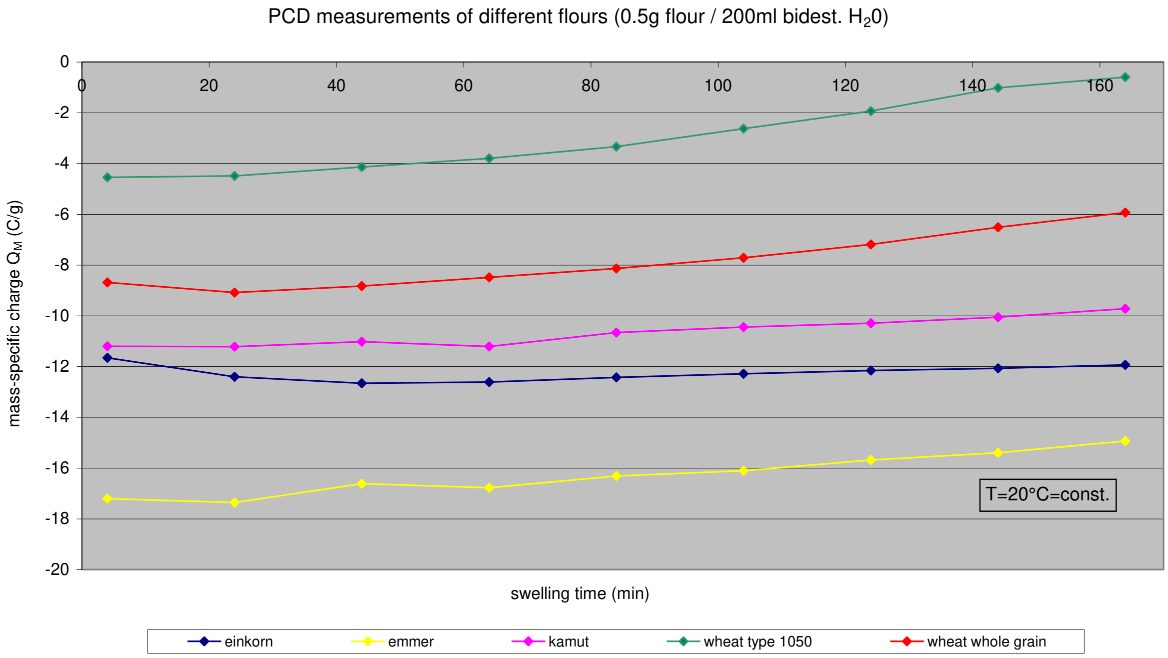

Fig. 4: PCD measurements of different flours (mass-specific charge Q_M)

A comparison between the evolution of electric charges of a whole grain wheat flour as against the studied wheat flour type 550 (Fig. 5) reveals curves with similar kinetics (sigmoid dynamics). This fact might be explained by the similarity or relatedness of the two ground grain products. Sigmoid kinetics of this kind is not, however, typical of all kinds of the studied flours: the whole grain einkorn (triticum monoccum), for example, is characterised by a nearly linear curve of mass-specific charge vs. swelling time (Fig. 4). On the other hand, whole grain flour emmer (triticum dicoccum) exhibits extremely anionic characteristics, but tends to largely decrease its anionic charge along the swelling process. Similar results are obtained for the whole grain kamut (triticum turgidum subsp. polonicum) under test, though with different charge levels (see Fig. 4).

Additionally, PCD measurements serve to reliably identify the quality and ratios of flour blends.

The graphic Fig. 5 illustrates the mass-specific charges Q_M of wheat flour type 550 (harvested 2007) blended with maize flour at different mixing ratios. Evidently, charge measurements lend themselves to characterizing and determining the blending ratios of various different flours. Here again, the calculated charge is indicated with the sign preceding the measured streaming potential in order to denote the anionic nature of the flours under test.

The data in Fig. 5 is indicative of an evolution or change in the mass-specific charge of the tested wheat flour type 550 along the swelling time, which is analogous to that of wheat flour type 1050. However, the studied wheat flour type 550 initially carries a less pronounced anionic charge (-1.5 C/g) which clearly shifted toward the cationic range in the course of investigations. The shape of the curve suggests that a finite electric condition has not yet been attained (measurements were prematurely abandoned after some 65 minutes). The lower bran content of flour type 550 might basically be responsible for the fact that, compared to flour type 1050, a smaller number of anionic charge carriers are initially present.

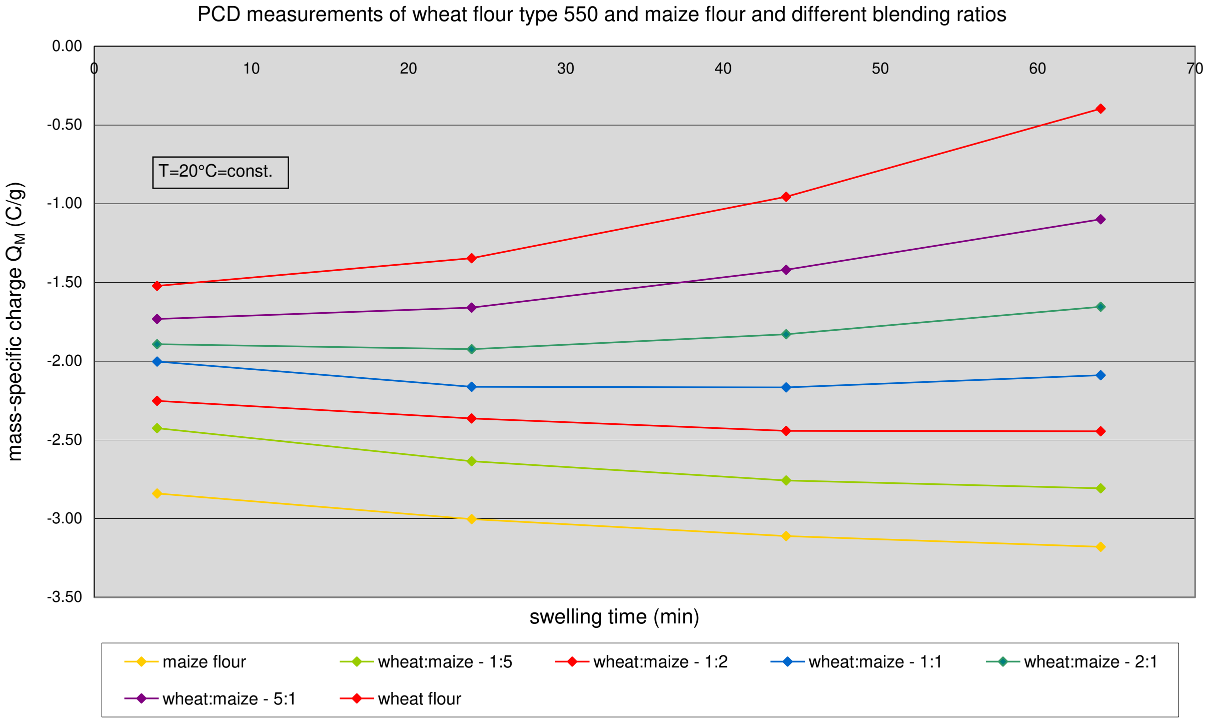

Fig. 5: PCD measurements of wheat flour type 550 (harvested in 2007) with maize flour added at different blending ratios (mass-specific charge Q_M)

According to the findings shown in Fig. 5, pure maize flour as against wheat flour exhibits higher anionic charges and increases its anionic charge level during the swelling process. This demonstrates a basic difference between maize and wheat in terms of the electrical properties of their ground products: wheat flours tend to shift their charges toward the cationic range along the swelling process whilst maize increases its cationicity during swelling. This is one of the reasons why charge measurements enable a specific differentiation and characterisation of blends of the two flours. Fig. 5 underlines this observation, since specific charges are identified for various blending ratios. Users are thus able, for instance, to apply a suitable charge titration in order to identify unknown blends.

Commercial vital gluten products were also included in the measurements with a view to clarifying to what extent glutens impact the specific kinetics of charge reversal in swelling wheat flours or during dough development. Typically, there is a sigmoid evolution from initially anionic charges toward faintly anionic or faintly cationic charges.

It may furthermore be assumed that ionic additives may impact the development of wheat dough or the charge household of a wheat flour / water suspension during the swelling process. With a view to characterising DATEM (diacetyl tartaric acid ester of monoglyceride) by charge measurement, the substance was studied with regard to its interaction with vital gluten on the one hand and wheat flour on the other. The results obtained are summarised in Fig. 6.

Evidently, the studied wheat flour type 550 (harvested in 2009) initially showed approx. -1.8 C/g before it underwent a distinct charge reversal which, under the test conditions chosen, reached a finite state at +0.3 C/g after about 120 minutes. After introducing into the wheat flour 1 % DATEM related to the amount of flour, repeated measurements revealed a change in its electrical properties. As flour components reacted with DATEM, an initial charge of approx. -1.8 C/g was observed. Interestingly, DATEM produced a very small change in the charge level which, as early as after 80 minutes, reached a finite end value in the faintly anionic range at approx. -0.3 C/g. It may be concluded that the above charge reversal occurring in freshly harvested and untreated wheat flour type 550 is prevented by interaction with, and in the presence of, DATEM (Fig. 6). Relying on his own studies and deliberations, Prof. Dr. Peter Köhler arrived at a similar conclusion (P. Köhler; Untersuchungen zur Backwirksamkeit von DATEM und seinen Komponenten; Getreide, Mehl und Brot 53 (1999)). Based on his data, Prof. Dr. Peter Köhler predicted a cationic charge of gluten contained in wheat flour which would be "neutralised" by DATEM. Our own studies applying PCD measurements have experimentally confirmed this assumption.

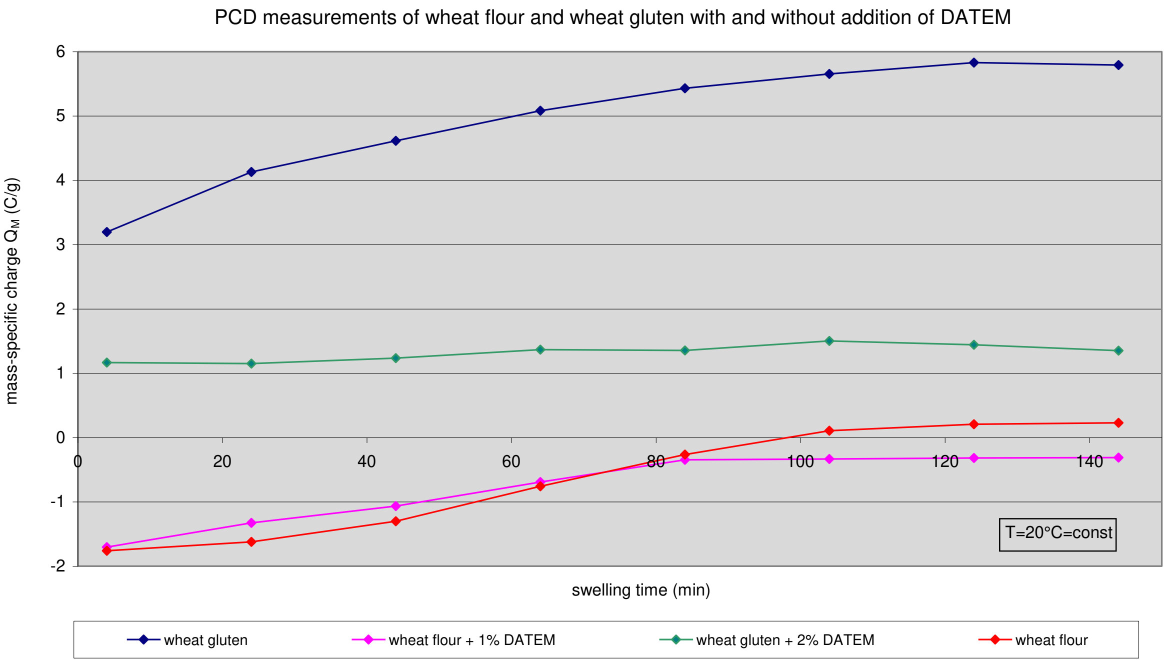

Fig. 6: PCD measurements of wheat flour and wheat gluten with and without addition of DATEM (mass-specific charge Q_M)

The measuring values shown in Fig. 6 demonstrate that wheat flour initially exhibits an anionic charge that is reduced along the swelling process before entering the cationic range after approx. 100-120 min. Pure wheat gluten by contrast shows a distinctly cationic charge of approx. +3 C/g at the onset of the swelling process and undergoes a slight charge increase to +5.8 C/g in a hyperbolic curve during the swelling period. Obviously, the charge of wheat gluten tends to shift toward the cationic range similar to the charge of wheat flours – though in a sigmoid rather than hyperbolic form. It follows that a certain relationship may be derived between the electro-functional properties of the gluten which might cause the charge reversal of wheat flour during its swelling in an aqueous medium.

In any case, additions of DATEM to wheat flour and wheat gluten decrease the charge which, however, keeps more constant along the swelling time: in the case of gluten, DATEM produces a lower cationic charge of approx. +1.2 to +1.5 C/g which remains nearly unchanged during the study period. After interacting with DATEM, wheat flour undergoes a similar modification of its electrical properties, since in this case mainly the anionic charges are substantially reduced which were measured as initial value at the onset of swelling. In the presence of DATEM no charge reversal takes place.

Taking the known baking properties of DATEM in wheat flours and wheat doughs into consideration, the desirable attributes of wheat flour are determined, among others, by the surface charges of ground products which are faintly anionic, without any charge reversals occurring during dough formation and dough development.

Summary and conclusions

Lengthy and complex measurements are frequently required to characterise ground grain products. Measurements with the Mütek PCD Particle Charge Detector by comparison are quick, simple and represent a novel method for charge characterisation of these ground grain products.

In the PCD measuring cell a streaming potential is measured which shows the charge sign of the sample. Anionic samples generate an anionic streaming potential in the cell whilst cationic samples produce a cationic streaming potential. The charge of a sample is identified via polyelectrolyte titration using a polyelectrolyte solution with opposite charge. Based on the streaming potential measured, the titration end point is determined. Once the streaming potential is at 0 mV, the titrant has neutralised the sample charge and the titration process is finished.

As charge measurements of different types of flours have confirmed, this method enables users to distinctly differentiate between individual flours and to reliably identify the blend quality and the blending ratios of flour blends.

In addition, the investigations have revealed a relationship between the milling yield of flours and the charge level: the higher the bran content, the higher the mass-specific anionic charge will be.

It appears the formation of wheat dough is generally accompanied by a charge reversal, i.e. a dynamic anionic-to-cationic charge change. This phenomenon can be prevented by adding, e.g., DATEM of mono- and diglycerides of food fatty acids. Generally speaking, the above and similar studies allow relevant conclusions as to the functional properties of this emulsifier within wheat dough systems.

This novel method for identifying the charge household in interacting systems may open up new possibilities of characterising ground grain products and may enable prognostications of functional properties of a variety of foodstuffs. Basic analytics of the effects of additives in dough or foodstuff systems may contribute toward a better understanding and/or clarification of chemical reactions or ionic interactions during many process steps.

Literature

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