THE CHARGE TITRATION - A QUICK ALTERNATIVE TO THE FORCING TEST

CONTEXT

Product stability is an important quality feature for the beer industry. To analyse the stability of the product, the physico-chemical properties are of particular importance. One of the quality problems is the premature clouding of filtered beers. To analyse this turbidity, the very lengthy forcing test was previously carried out. If beer is now considered to be a colloidal dispersion, then colloid chemical measuring methods such as dynamic light scattering (DLS) or flow potential in conjunction with charge titration can be used.[1,2]

FLOW POTENTIAL AND CHARGE TITRATION

Whether the interface is a flat, a particle or a molecular surface, the same laws apply to all of them. A charged surface attracts excess ions with opposite polarity from the liquid environment, which shield the charge from the outside.

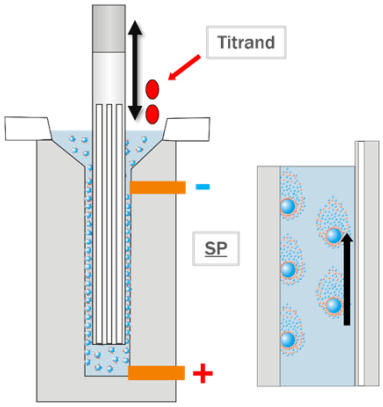

Figure 1: Setup of the STABINO ZETA. Oscillatory displacement of the ion cloud around the particles adhering to the porous walls of the PFTE sample container and flask by the up and down movement of the displacement flask. The resulting oscillating charge cloud is tapped as a sinusoidal flow potential SP at the two electrodes.

The loosely bound ions of the charge cloud (double layer) can be sheared off by an electric field or by mechanical work (flow). The potential that forms on the shear layer can be measured with the STABINO ZETA. There, the sample is set in motion in a kind of capillary, and the charge cloud is shifted in the direction of the flow, resulting in the flow potential (proportional to the zeta potential).

During charge titration with polyelectrolyte solutions, the charge of the particles is neutralized, and thus the total charge is determined. The zeta potential/flow potential is a measure of the stability of a dispersion, i.e., the higher or lower the potential or the titrated charge quantity, the more stable the dispersion. ***Figure 1*** shows the setup of the STABINO ZETA measurement.

REALISATION

In order to determine the turbidity or colloidal stability of filtered beers, charge titrations were performed with the charge-calibrated cationic polyelectrolyte 0.001 N P-DADMAC (polydiallyl dimethylammonium chloride). To obtain a comparison to the forcing test, it was carried out in parallel. In the forcing test, a charge titration was carried out after each warm day, and the turbidity was measured at a 90° angle in EBC formazine units. [3, 4]

MEASUREMENTS RESULTS

The titration curve of the measured flow potential (ψ) shown in ***Figure 2A*** is approximated by a mathematical function, as shown in ***Figure 2B***. By calculating the first and second derivatives of this function, a local minimum at -284 mV and 0.43 ml can be calculated. [3]

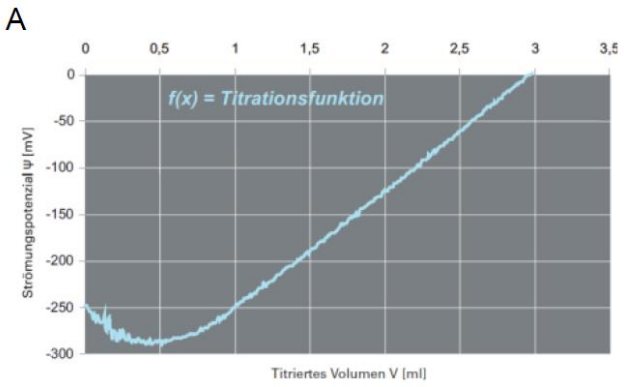

Figure 2A: Titration curve of filtered beer

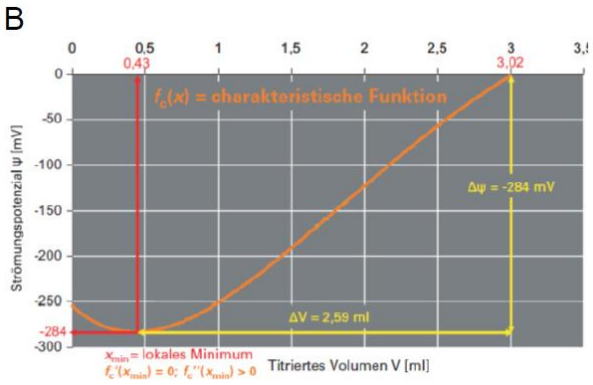

Figure 2B: Function of the titration curve with the local minimum and a zero at 3.03 ml 0.001 N P-DADMAC [3]

As described in the implementation, the flow potential and a charge titration were carried out on each warm day in parallel to the forcing test. Figure 3 shows the titration curves of the charge titration of a beer sample. [3]

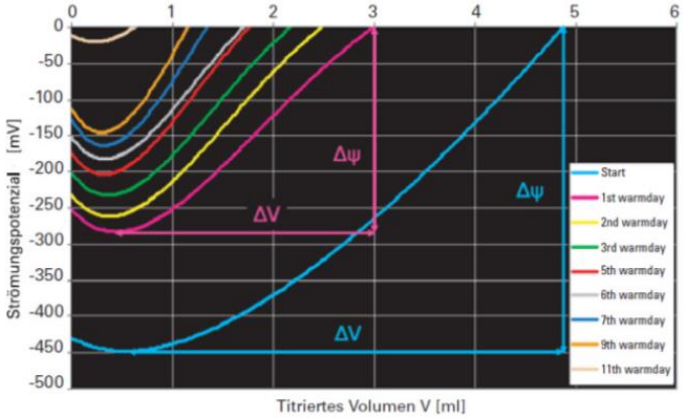

Figure 3: Titration curves of charge titration on each warm day. (taken from:[3])

The measurements all show the typical course of the titration curve as in the fresh beer sample. By calculating Δψ and ΔV for each titration curve, it becomes clear that both the flow potential and the consumed volume of P-DADMAC decrease with ageing. For comparison, ***Figure 4*** shows the turbidity curve of a filtered beer sample. Here, it can be seen that only very slight changes in the curve can be seen, especially in the first part of the curve.[3]

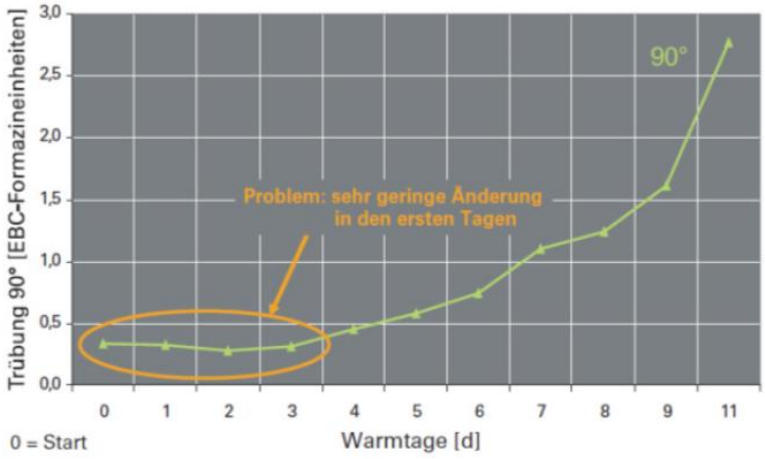

Figure 4: Measured turbidity curve of a filtered beer sample as a function of the warm days at a 90° angle. (taken from:[3])

The curves shown in ***Figure 5A*** show the titrated differential volume ΔV as a function of time and the turbidity as a function of time. Here, too, it becomes very clear that the change in volume is greatest at the beginning of the measurements, which is a clear advantage over the forcing test. [3]

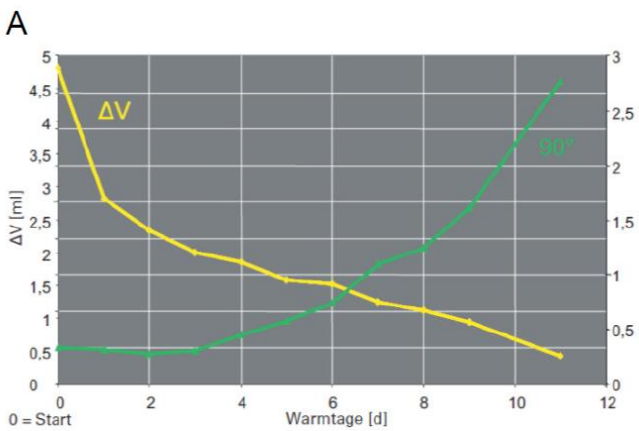

Figure 5A: Decrease in ΔV and increase in turbidity as a function of warm days.

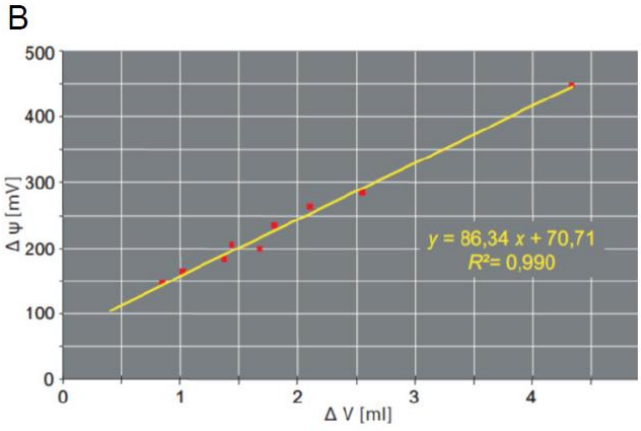

Figure 5B: Relationship between ΔV and Δψ as a function of the different warm days. (taken from:[3])

If the calculated differences QV of each warm day are ψ to the potential, this results in a linear relationship with R^2 = 0.990. This relationship is shown graphically in ***Figure 5B.***

This charge titration method shows that a single measurement is sufficient to assess the stability of the beer sample.[3]

SUMMARY

In contrast to the forcing test, charge titration can be used to obtain information about the stability of the beer very quickly. A single measurement (approx. 5 – 10 min) can be used to assess stability before storage. Furthermore, there are other interesting applications for flow potential and charge titration.

These possibilities include the predictability of gushing, as well as the rapid determination of nitrogen compounds during wort boiling.

LITERATURE

- [1] TITZE, J., CHRISTIAN, M. 2010: Combined Particle Analysis – A Novel Method in Brewing and Beverage Analysis. Getränkeindustrie **64** No. 10, pp. 52-55.
- [2] TITZE, J., ILBERG, V., JACOB, F., PARLAR, H., 2008: Possible applications of the charge titration method for the assessment of chemical-physical beer stability, Part 1. Brauwelt **148,** No. 18/19, pp. 506-509.
- [3] TITZE, J., ILBERG, V., JACOB, F., PARLAR, H., 2008: Possible applications of the charge titration method for the assessment of chemical-physical beer stability, Part 2. **23,** pp. 624-527.
- [4] TITZE, J., CHRISTIAN, M., ILBERG, V., JACOB, F., 2010: Particle analysis – A combined method to analyze the colloidal characteristics of particles. BrewingScience **63,** Nr. 5/6, S. 62-71.