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ABOUT THE INFLUENCE OF METAL IONS ON THE STABILITY OF FRANKFURTER TYPE SAUSAGES AND THE EFFECT OF CITRATE

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SUMMARY

The influence of metal ions (Ca-II, Mg-II and 9 transition elements with various electric charges) in concentrations up to 10^{-2}M was studied in cooked sausages batters (frankfurter type) prepared from postrigor beef, and pork back fat containing 2% salt. Also the effect of a further addition of 0,3% sodium citrate (1.1×10^{-2}M) was investigated. Ca-II and Mg-II did neither influence the batter stability nor the effect of citrate which reduces jelly and fat release in cooked batters by about 30%. On the addition of 5×10^{-4}M of transition metal ions Ag-I ions increased the jelly plus fat separation in cooked batters without citrate by 100%, Cu-II by 55%, Cd-II by 35%, Fe-II and Co-II by 20%. Bivalent cations of Hg, Zn, Pb, Ni, and Fe, and Cu-I showed no effect. 10^{-2}M of these ions increased the separation in all cases by 30-100%. By the addition 1.1×10^{-2}M citrate the cookout in batters containing 10^{-2}M Ni-II, Fe-III, and Co-II was reduced. In all other cases citrate had none or a limited effect only. The mode of action of the metal ions is not fully solved. Promotion of oxidative processes may be involved. Citrate which binds metal ions counteracts their action partially.

INTRODUCTION

Meat contains metal ions in a wide range of concentrations and with different function. Ca-II ions (about 10^{-3}M) are needed during muscle contraction, Mg-II (about 10^{-2}M) are involved in processes of energy turnover, Zn (10^{-3}M), in hydrolytic processes Fe (4×10^{-4}M) and Cu (5×10^{-5}M)-ions are factors in oxidative processes. Other transition-element ions occur in meat usually in concentrations of 10^{-6}M and lower. During processing, however, a carry-over from spices, additives and salt may occur or particles of metal oxides or elementary metal from the processing machinery may be transferred into the batter.

Citrate is known to bind a number of cations. As a hypothesis of its mode of action in cooked sausage the binding of Ca-II is widely assummed and by this binding of Ca-II ions the water and fat binding of cooked sausages shall be enhanced. Indeed the addition of 0,3% citrate (1.1×10^{-2}M) reduced the jelly and fat separation of cooked sausages by about 30%. In the literature the pK value for Ca-citrate is reported to be 3.2 (MEITES, 1963) and 3.9 (HAMM, 1956). These pK values are valid usually in the alkaline pH region only. With a concentration of Ca-II in muscle of about 10^{-3}M, the free Ca-II concentration after the addition of 10^{-2}M citrate would be at alkaline pH about 7×10^{-5}M. HAMM (1956) reports, however, that at pH values of the batter between pH 5.5 and 6.5 only 60 to 73% of the Ca-II is bound to citrate. That means in post rigor meat provided all Ca-II are free to be bound to citrate the concentration of free Ca-II would be about 0.4×10^{-3}M. During the development of rigor mortis 10^{-5}M Ca-II is sufficient to form actomyosin. Therefore the hypothesis for the mode of action of citrate by binding of Ca-II in order to improve the batter stability seemed us to be doubtful. Furthermore if Ca-II binding is essential for the batter stability the complexing agents EDTA or EGTA with high Ca-II binding ability should also enhance batter stability. But they don't do so. Thus the effect of citrate remains uncertain.

As mentioned above other ions occur in meat. Zn-II and escpecially Fe-II and Fe-III which are involved in oxidative processes, are rather common. Therefore we investigated the effect of these ions and those of other transition elements on batter stability and the action of citrate in the presence of these ions.

MATERIALS AND METHODS

Preparation of sausages

450 g post rigor lean beef was comminuted in a 2 l bowl cutter for 20 sec. Then 450 g crushed ice, 18 g salt containing 0.1 g $NaNO_2$ and if applicable 2.7 g Na-citrate or metal salts of various amounts were added and comminuted for further 160 sec. The temperature of the batter was kept below 6°C by the addition of liquid nitrogen. After the addition of 200 g of ground pork back fat the comminution continued for further 180 sec. The maximum temperature at the end of comminution was about 12°C.

200 g of batter were filled in cans, closed and heated for 35 min in a boiling water bath (core temperature about 90°C). After cooling in running tap water, the cans were stored at 0°C for 24 hours.

Determination of centrifugation loss

10 g of raw, fat containing batter were weighed in a centrifugation tube and centrifuged at about 45,000 xg for 30 min at 2° to 5°C. The fluid collecting on top of the batter was decanted and the remaining batter was reweighed. Centrifugation loss is expressed as percent of the original weight of batter.

Determination of cooking loss

Before the addition of pork fat to the batter 400 g of "fat-free" batter was removed from the mixture, filled in cans and heated and cooled as mentioined above. After 24 hours the cans were warmed up in 45°C water for 1 hour, opened and the fluid jelly was measured with a measuring cylinder and calculated as percent of the original weight. This we call cooking loss of "fat free" batters.

Determination of jelly and fat separation

The pork fat containing comminuted batters were treated for determination of jelly and fat cookout as described for cooking loss. The fluid jelly and fat separated well in the measuring cylinder and were calculated as percent of original weight of batter.

Composition of batters

The "fat-free" batters contained approximately 85% water, 11% protein, 2% fat and 2% salt. The fat containing batters contained approximately 63% water, 9% protein, 27% fat and 1,8% salt.

RESULTS AND DISCUSSION

1. The effect of Ca-II and Mg-II

The addition of 3×10^{-3}M Ca-II or 10×10^{-3}M Mg-II to batters showed no effect on cooking loss, jelly and fat separation. Addition of 0,3% citrate (1.1×10^{-2}M) lowered the jelly release of the batters

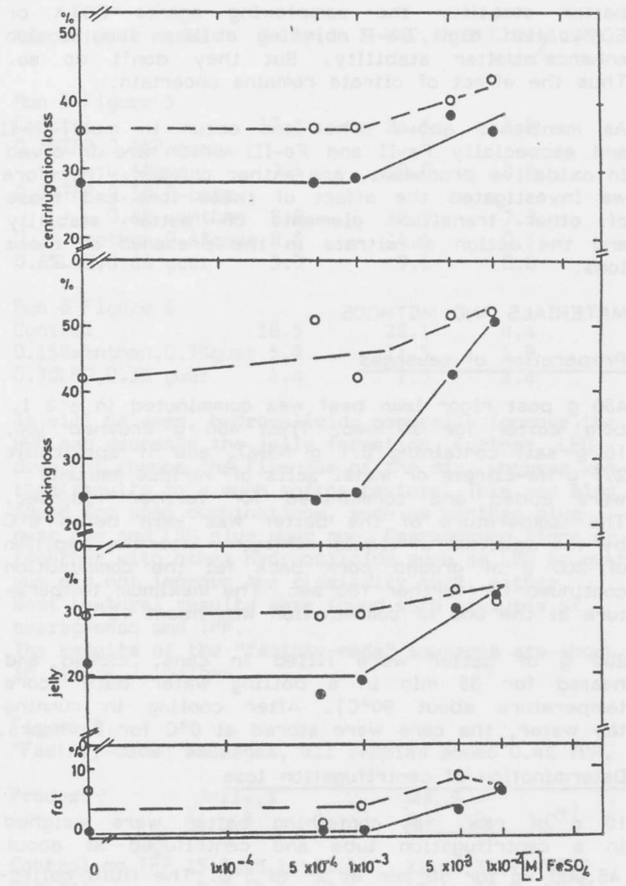


fig. 1 Effect of Fe-II ions on the stability of batters without (o) and with (•) 0,3% (1.1×10^{-2} M) citrate. For details see Material and Methods.

by about 30%. Ca-II or Mg-II ions in these batters had no influence on batter stability. 2.3×10^{-3} M EDTA or 12.5×10^{-3} M EGTA had no effect either on batter stability without citrate. As Ca-II and Mg-II additions do not reduce the effect of citrate, and the Ca-II binding compounds EDTA and EGTA do not improve the batter stability either we conclude that the enhancement of batter stability by citrate cannot be due to Ca-II or Mg-II binding.

2. The effect of Fe-II and Fe-III

Fe-ions in meat are bound mainly to myoglobin. Beef contains about 4×10^{-4} M of iron which exists as myoglobin with Fe-II and metmyoglobin with Fe-III. We studied the effect of both Fe-salts. Additions of Fe-II or Fe-III increase without citrate the centrifugation - and cooking loss slightly, also jelly and fat separation (fig. 1 and 2).

In batter with 1.1×10^{-2} M citrate and Fe-II concentrations below 10^{-3} M all losses and cookouts were reduced considerably. Above 10^{-3} M Fe-II the effect of citrate decreased (fig. 1). At 10^{-2} M Fe-II, equivalent to the citrate concentration the batters with or without citrate had the same water and fat release.

Addition of Fe-III in the presence of citrate lead to different results. The centrifugation loss did not change (fig. 2). Cooking loss and fat separation increased slightly. With jelly release the effect of Fe-III was somewhat more pronounced. There

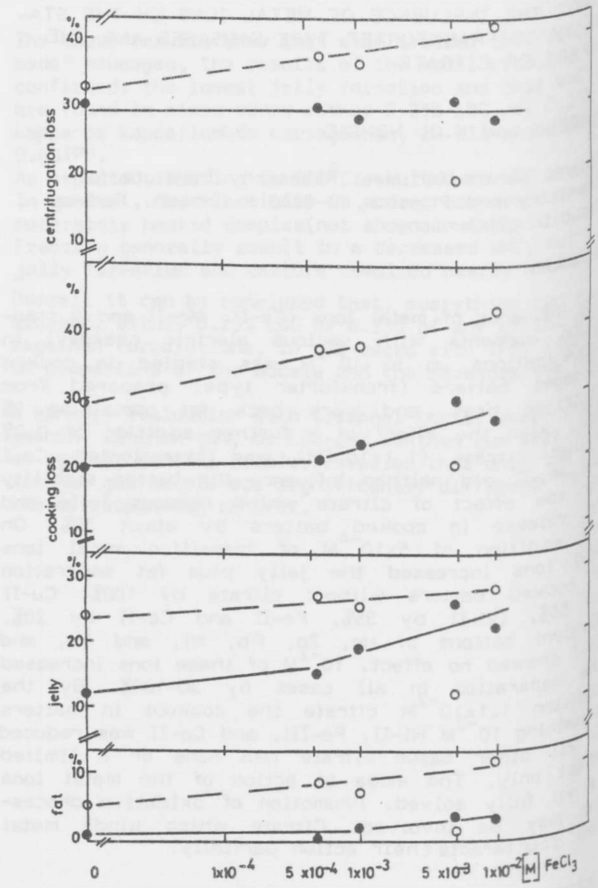


fig 2 Effect of Fe-III ions on the stability of batters without (o) and with (•) 0,3% (1.1×10^{-2} M) citrate. Details see in Materials and Methods.

is a difference between Fe-II and Fe-III: Citrate binds Fe-III (pK 11.8) much more tightly than Fe-II with a pK of 3.1 (MEITES, 1963). This may explain the different behaviour of these ions in the presence of citrate. Without the addition of citrate the changes however are very similar (fig. 1, 2). Fe-III ions are able to oxidize certain groups like SH-groups in proteins or promote C=C double bonds oxidation in the presence of oxigen. Fe-II may be oxidized by the oxigen in the batter to Fe-III. By the binding of Fe-III by citrate the oxidative properties may be inhibited especially in the unheated batter (see centrifugation loss in fig. 1, 2) but also partially in the heated batter.

3. The effect of Zn-II

Zn-II is a rather common cation (10^{-3} M) in meat. It is known as a cofactor for several enzymes. Zn-II addition to batter shows a strange behaviour of its binding ability. Up to 10^{-3} M Zn-II ions reduce considerably centrifugation loss, but have no effect in heated batters. With 10^{-2} M Zn-II the centrifugation loss is again as high as without Zn-II; the cooking loss increases at 10^{-2} M Zn-II by 10.0% the jelly by 20.0% and fat separation amounts to 9% absolute from 0.5% without Zn-II addition. With 0,3% citrate in the batter the centrifugation loss decreases again at 10^{-3} M Zn-II increasing again with 10^{-3} M Zn-II to its level without Zn-II addition. Cooking loss, jelly and fat release are unaffected by 10^{-3} M Zn-II; at 10^{-2} M Zn-II the batters with

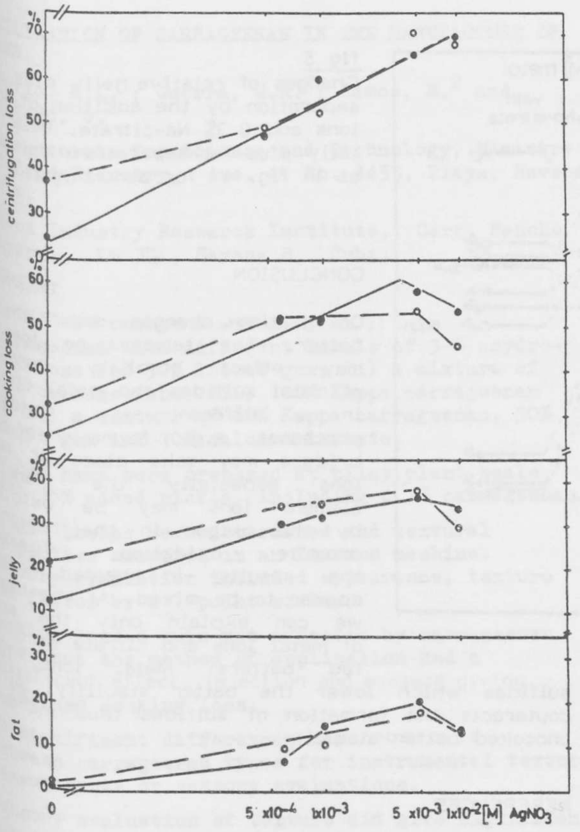
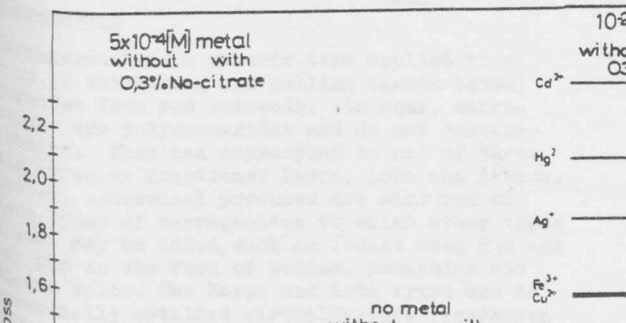


fig 3 Effect of Ag-I ions on the stability of batters without (o) and with (●) 0,3% (1.1×10^{-2} M) citrate. Details see in Materials and Methods.



citrate show a sharp increase in the cookouts up to levels of the batters without citrate. We have no explanation for these results yet.

4. The effect of Cu-II and Ag-I

Cu-II and Ag-I ions (fig. 3) increase the jelly release already at low concentrations. In concentrations of 5×10^{-4} M the jelly plus fat release is enhanced by 55% with Cu-II and 95% with Ag-I. Citrate addition abolishes the action of Cu-II, but with 5×10^{-4} M Ag-I there is still an increase in jelly plus fat of 65%. At 10^{-2} M Cu-II and Ag-I ions there is no effect of citrate on batter stability. These results were obtained with cooked batters. In unheated batters Ag-I ions show again a similar effect (fig. 3) with little effect by the addition of citrate. But 5×10^{-4} M Cu-II does not increase centrifugation loss and addition of citrate lead to an reduction of jelly and fat release by about 30%. There exists a difference in uncooked and cooked batters with Cu-II. Ag-I ions, which are not bound to citrate, are known to bind very tightly to SH- groups; therefore citrate has no effect of Ag-I addition, which may inhibit the formation of S-S bridges in batters.

5. The effect of transition elements on centrifugation loss

If there is a binding to SH-groups involved in the action of the transition metal ions, then those ions which form stable metal sulfides should show the biggest effect in batters. Fig. 4 shows that this indeed happens in unheated batters. 10^{-2} M metal ions of Cd-II, Hg-II, Ag-I, Fe-III and Cu-II increase centrifugation loss considerably.

The ions which form weak metal sulfides like Ni-II and Co-II show no effect. This indicates the formation of metal sulfides in the unheated batter, reducing its stability.

fig. 4
Changes of relative centrifugation loss by the addition of metal ions and 0,3% Na-citrate. Relative centrifugation loss: centrifugation loss of batter with metal ions and/or citrate divided by centrifugation loss of batters without metal ions and without citrate.

Addition of 10^{-2} M citrate reduces centrifugation loss in nearly all cases but not with Ag-I. Most effective is citrate on the Fe-III ions which belong to those metal ions which bind tightly to citrate. Citrate seems to counteract the metal sulfide binding in the unheated batter, improving by this action the batter stability.

6. Effect of transition elements on heated batters

In heated batters - jelly plus fat separation are shown in fig.5 - the metal ions behave differently. With low metal ion concentrations (5×10^{-4} M) the increase in relative cookout is considerably higher than in the unheated batter (fig.4). Again Ag-I ions are most effective. But the sequence of metal ions on their action on batter stability changes. In a concentration of 10^{-2} M Ni-II, Fe-III and Co-II are the least effective on cookout, in unhea-

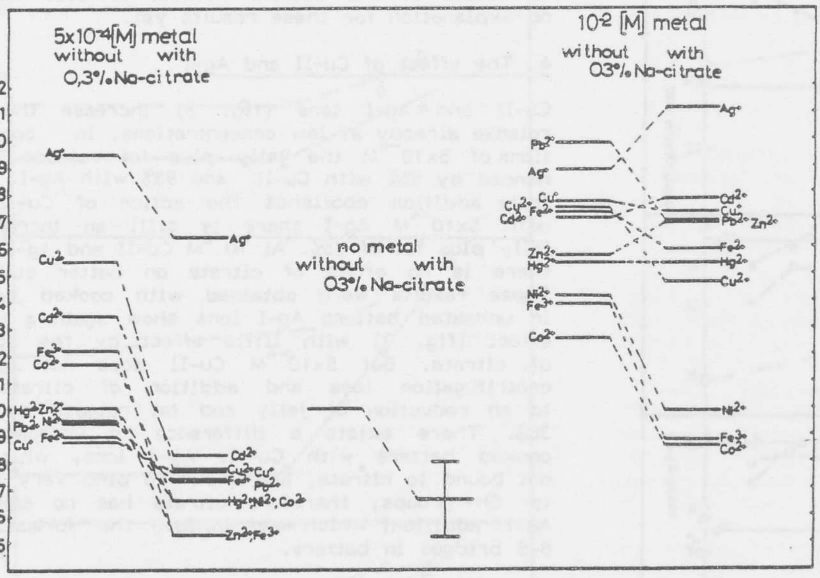


fig 5
Changes of relative jelly plus fat separation by the addition of metal ions and 0.3% Na-citrate. Relative jelly plus fat separation: calculated as in fig. 4 for centrifugation loss

ted batters Fe-III was rather effective. The highest cookout exhibit the batters with Pb-II, Ag-I, Cu-I and II, Cd-II and Fe-II. The batters are little affected by the addition of citrate except by the simultaneous addition of Ni-II, Fe-III and Co-II but also Pb-II and Cu-II. The latter bind tightly to citrate.

CONCLUSION

On heating changes occur in the batter. The temperature increase may effect stability constants of metal sulfides and metal citrates in a different way. Oxidative processes e.g. formation of S-S-bridges may take place or metal ions especially the transition element ions may be oxidized by the oxigen in the batter or promote oxidation. Therefore the results in heated batters appear to be mixed. At the moment we can explain only the action of metal ions and citrate in unheated batters: Metal ions form sulfides which lower the batter stability, citrate couteracts the formation of sulfides thus increasing uncooked batter stability.

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