Errors in pH Measurement of Meat and Meat Products by Dilution Effects

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SUMMARY

PH values measured with a spear-tip electrode directly in a meat sample differ significantly from pH measurements of meat homogenate diluted with deionized water. The water causes an unacceptable shift of pH as high as +0,25 to -0,3 pH at ratio 1 : 10 (w/v). The error increase relates to the amount of water added and to the distance to the isoelectric point. The measurement error can be minimized or completely eliminated if a sodium chloride solution of 1,0 to 1,5 % NaCl for meat and 5 to 6 % for sausages is added instead of water. The added salt solution should have the equivalent ionic strength as the original sample.

INTRODUCTION

The pH of meat and meat products is considered to be one of the more important factors to judge, water-holding capacity, microbial stability, binding properties and carcass quality characteristics.

Two main methods of pH determination are widely accepted: (1) homogenizing the sample (if necessary with dilution) and measuring in the homogenate (§ 35 LMBG) and (2) direct measurement using a spear-tip electrode. But literature shows, that most researchers using the homogenization method, do not keep to the official methods (§ 35 LMBG, ISO 2917, DIN 10146). They use varying solvents as well as varying sample/ solvent ratios (from 1 : 1 up to 1 : 10 (w/v)), to adjust the method to their specific needs. This adds a measurement error to the homogenization method which is not found with the direct method (2). This observation is in line with previous research documenting comparable deviations of pH related to varying dilutions (DEMEYER, 1979). The objective of the present study is to determine the pH deviation related to the sample/ solvent ratio and to indentify a solvent, which does not influence the initial pH.

MATERIALS AND METHODS

PH measurements were made with a spear-tip penetrating glass-electrode (Xerolyt, LoT-406-M6-DXK-S7, Ingold, Steinbach, FRG), attached to a microprocessor pH meter WTW 537 (WTW, Weilheim, FRG). The influence of temperature was automatically compensated by a temperature sensor TFK 150 (WTW) in the sample or the homogenate. The pH meter calibration was checked according to the instructions of the manufacturer in regular intervals with buffer solutions 4,01 and 6,86 (Ingold). Measurements were carried out at room temperature. The sample was cooled with ice-water, if necessary.

Beef, pork, turkey and a variety of sausages were purchased in local shops. To cover the different types of sausages a dry sausage (Salami), a finely comminuted spreadable liver sausage (Kalbsleberwurst) and a emulsion-type sausage (Fleischwurst) were used. The meat was free of visible fat and connective tissue. A few hundred grams of each sample were finely comminuted in a Moulinette (Moulinex), to get a standardized mixture. At the beginning of each series of measurements a 10 g sample was taken from the mixture and again homogenized with an Ultra Turrax (Janke & Kunkel, Staufen, FRG). The pH was then measured. Five readings were taken within the homogenate and the average was taken as the initial or "true" pH. The sample was then diluted with 2 ml of solvent, homogenized and measured again. This procedure was continued through the following dilution steps: 2, 4, 8, 10, 15, 20, 30, 50, 100, 200, 300 and 500 ml. So at the end of each series the 10 g sample was diluted in 500 ml of solution.

The salt solutions were prepared with sodium chloride p. a. (Merck, Darmstadt, FRG). It should be pointed out that only the use of sodium chloride p. a. grade (ACS, ISO Standards) is recommandable to prepare a salt solution, because common table salt often contains anti-caking agents such as silicates or calcium carbonate which can change the buffering capacity leading to unpredictable effects.

To achieve a lower initial pH-value of the meat, the 10 g samples were mixed with different amounts of glucono-delta-lactone (GDL) and held overnight in a refrigerator at 5 °C. After that the pH had reached a stable value and was measured using the same procedure as before. GDL was chosen, because the dry crystals do not change the initial water content of the samples.

RESULTS AND DISCUSSION

The influence of adding deionized water on the pH of beef is given in Fig. 1. The curves obtained with pork and turkey showed a similar shape and the deviations were in the same order of magnitude. At higher initials values (pH > 5,5) the pH constantly increased with increasing amount of water, whereas at lower initial values (pH < 5,4) the pH constantly decreased. At about 5,45 the pH did not change at all, regardless of increasing dilution. A distinct difference was observed especially after the addition of the first few milliliters of water. The maximum error at ratio 1 : 10 (w/v) could be as high as +0,25 and -0,3 pH, respectively. This is not a reliable pH measurement. Prior to the study single variable testing for kind of water (deionized, distilled, bidistilled), kind of acid (GDL or lactic acid), degree of homogenisation and time for reaching equilibration showed no significant influence on the observed deviations. The error in pH measurement depended not only upon the amount of added water, but also upon the initial pH, which is plotted in Fig. 2. The lowest deviation for all meats was obtained at pH 5,43 to 5,5, whereas the highest deviation was observed at high (pH > 5,7) and low (pH < 5,0) initial values. The same behaviour as with meat was found with the different sausages. The pH of the finely comminuted spreadable

Fig. 1: Influence of deionized water on the pH of beef. The initial pH (0 ml) was chemically adjusted with GdL. Sample size: 10 g

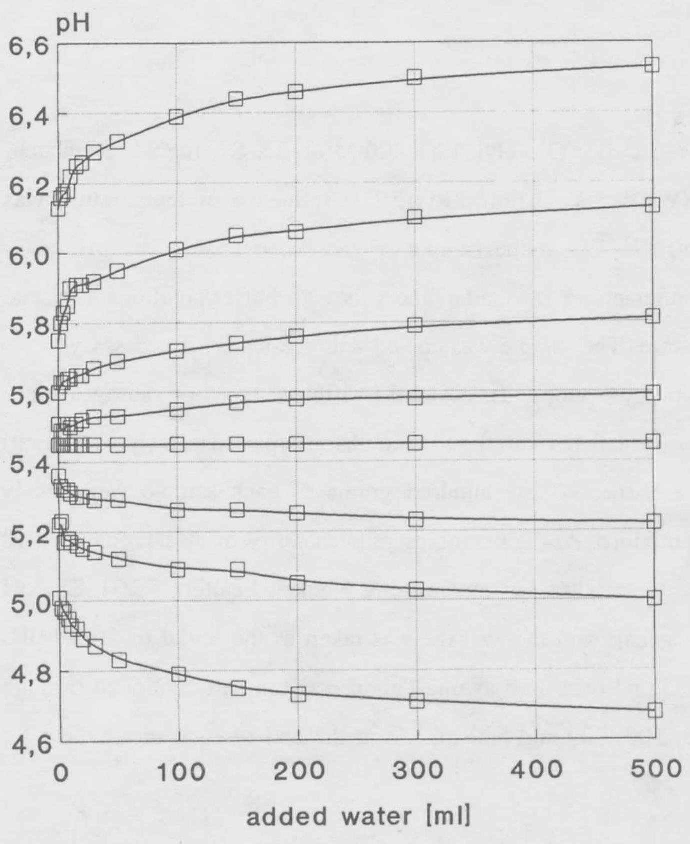
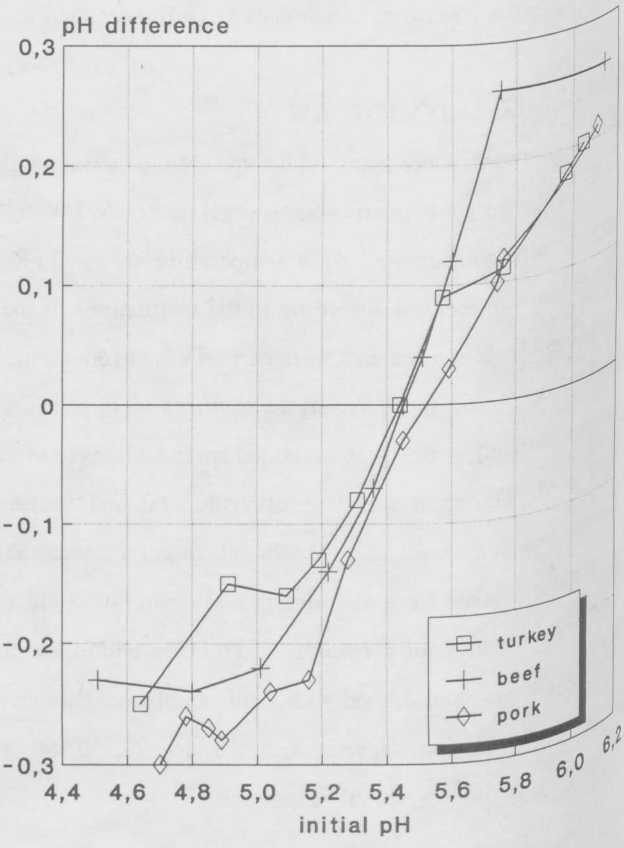


Fig. 2: Influence of deionized water on the difference from initial pH to measured pH at ratio 1:10 (w/v). Solvent: deionized water; sample size: 10 g



liver sausage (pH 5,87) increased by 0,13, the emulsion-type sausage (pH 5,75) by 0,17 and the pH of the dry sausage (pH 5,06) decreased even by 0,35 units.

The pH shift of the diluted homogenates is a result of added water. Any further addition of water dilutes the system and lowers the ionic strength. This alters the pKs of the meat buffers (BENDALL, 1973). More or less of the basic protein groups dissociate and change the net charge of the proteins. This changes the hydration of the proteins and therefore the pH of the meat homogenate (HAMM, 1972). The direction of shift depends on whether the initial pH is higher or lower than the isoelectric point (pI) of the product. (The pI itself depends mainly on the ionic strength and thus on the content of salts.) The influence of water and salts is the lowest at the pI, because the net charge is near zero and the total charge is at the maximum. Therefore it is assumed that the pI of the beef sample was at pH 5,45 (Fig. 1).

HAMM reported already in 1957 on the effect of neutral salts on mammalian muscle. He stated that in contrast to a dilution with water, added NaCl had a reverse effect on the dissociation of muscle protein. The idea of using a sodium chloride solution instead of deionized water was developed from his theories, to suppress the unintentional shift in pH due to dissoziation effects. The influence of added NaCl solutions of different concentrations on the pH of pork can be seen in Fig 3. By using a NaCl solution with a concentration of 1 to 1,5 % the lowest deviation to the initial pH was obtained, regardless of the amount of solvent. An increase in salt concentration beyond this limit worsened the deviation. The pH of beef also remained unchanged with the addition of a 1 to 1,5 % NaCl solution (Fig. 4). While the most favourable concentration to get stable values for both cooked sausages was around 5 to 6 % NaCl, the dry sausage gave the smallest deviation with 7 % NaCl. Still, a difference of -0,15 pH was left.

The positive effect of sodium chloride solutions on pH measurement can probably be explained by the constant ionic strength in the diluted sample. Hence it follows that the ionic strength of the meat or meat product must not be altered by the solvent.

Fig. 3: Influence of sodium chloride solutions of different concentrations on the pH of pork. Standardized to an initial pH of 5,92; sample size: 10 g

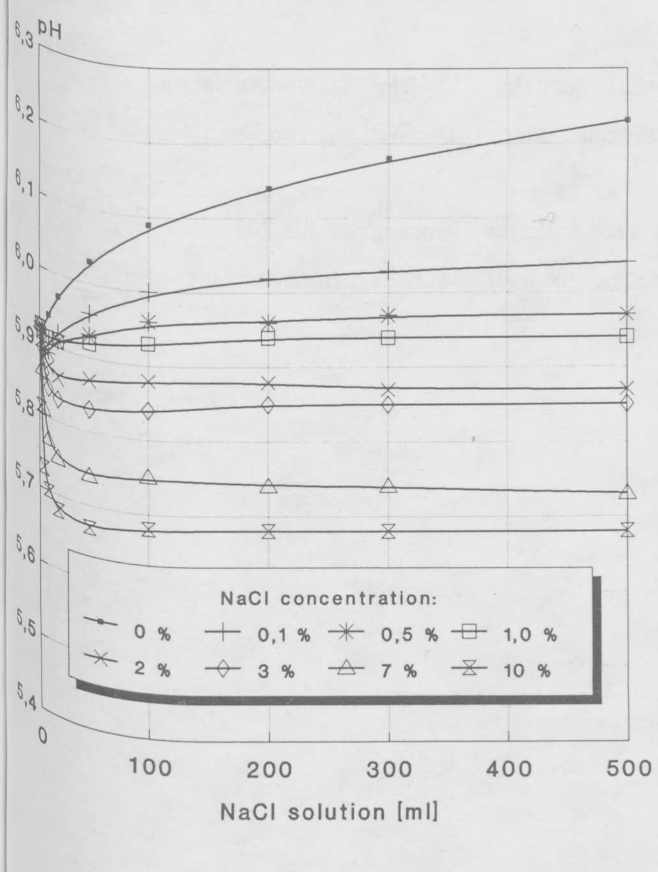
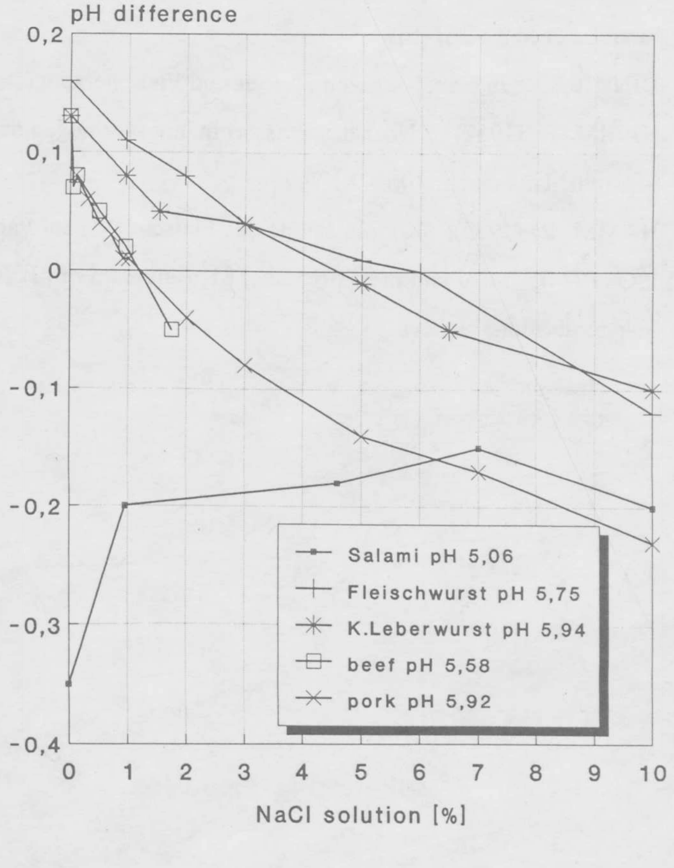


Fig. 4: Influence of sodium chloride solutions of different concentrations on the difference from initial pH to measured pH at ratio 1:10 (w/v). Sample size: 10 g



This can be achieved by using a sodium chloride solution of the same ionic strength as the sample. Bendall (1973) reported that the ionic strength of a 150 mM potassium chloride solution ($\mu = 0,15$) is equivalent to that of mammalian muscle. This confirms results, because the 1 % NaCl solution (172 mM) corresponds to a ionic strength of $\mu = 0,17$.

CONCLUSIONS

Excessive dilution of a meat homogenate with deionized water prior to pH measurement, causes an unacceptable shift of the initial pH, due to the change of ionic strength. The error increases with increasing addition of water. Therefore the measurement directly in the meat homogenate without added water can be regarded as the most suitable method. If a dilution is unavoidable, the deviation can be eliminated or minimized by (1) using as less water as possible or (2) the use of a sodium chloride solution instead of deionized water. Thus the pH will become independent of the amount of added solution, which improves the precision of the method. While the concentration of 1 to 1,5 % NaCl (w/v) gives the lowest deviation with meat, the best concentration for sausages is around 5 to 6 %. This suggests that the optimum concentration of a salt solution would depend to a great extent on the ionic strength of the sample.

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