ASSESSMENT OF PORCINE MEAT QUALITY AT THE SLAUGHTER LINE USING RAMAN SPECTROSCOPY

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Abstract – Fresh intact porcine *semimembranosus* muscles (N=151) were measured between 30 and 60 min post mortem along the slaughter line of a commercial abattoir using a hand held device to determine the ability of Raman spectroscopy to predict meat quality. Technologically important quality traits such as pH_{35}, pH_{24} and drip loss (DL) were measured using classical reference analysis and they were correlated with the Raman spectra using partial least squares regression. Predicting pH_{35}, pH_{24} and DL yielded a coefficient of determination of 0.75, 0.58 and 0.83 and a root mean square error of cross validation of 0.09 pH-units, 0.05 pH-units and 0.6 %, respectively. For the models, Raman signals of energy metabolites such as lactate, phosphate, ATP and phosphocreatine were weighted. This is the first Raman spectroscopic study to measure and predict quality traits in intact muscles along the slaughtering process showing the potential of early postmortem Raman spectra to measure pH_{35} and to predict pH_{24} and DL.

Keywords – pH, drip loss, early postmortem, non-invasive

I. INTRODUCTION

Meat quality measurements are rarely performed in commercial abattoirs. The reason for this is twofold: (1) The established measuring techniques are either too slow, invasive, imprecise, and/or yield the results only days after slaughter and (2) the spectroscopic methods which were evaluated so far lack the accuracy and/or speed for an on-line assessment of meat quality traits along the slaughtering process.

On the other hand, the relationship between early postmortem metabolism and meat quality is well known and extends beyond extreme deviations such as PSE (pale soft, exudative) or DFD (dark, firm, dry) meat. For example, pH_{45} is correlated with the water holding capacity [1] and the early postmortem metabolism in porcine muscles was shown to influence pH_u, color, drip loss (DL) and shear force [2-6].

In this field, Raman spectroscopy has already been applied to measure the pH in porcine *semimembranosus* (SM) muscles by using only phosphate signals [7]. In addition, the most important spectral changes in early postmortem Raman spectra were assigned to energy metabolites such as lactate, glycogen, ATP and others [8]. Hence, the Raman spectra provide a metabolic fingerprint with the potential to predict the biochemical status. In a previous study, Scheier, *et al.* [9] have used a handheld device to measure and predict quality traits from Raman spectra which were measured between 1 and 2 h *post mortem*. The partial least squares regression (PLSR) models in this study were mostly based on Raman signals of energy metabolites.

However, for an application in abattoirs, the quality assessment has to yield results before the carcasses are entering the chiller. Therefore, in this study, a first attempt is made to apply a mobile Raman device to measure and predict important quality traits at the slaughter line of a commercial abattoir.

II. MATERIALS AND METHODS

Raman and reference measurements were performed as part of a larger study with 151 porcine *semimembranosus* muscles which represent a random sample of pigs slaughtered in Switzerland (48 slaughter batches of different origin).

Early postmortem Raman and pH measurements were performed along the slaughter line 25-60 min p.m. during the normal operation of the abattoir on four days. To this end, 3-5 carcasses at a time were moved from the main slaughter line to the veterinarian line. Then, 3-6 pH measurements were conducted 25-40 min p.m. using a

puncture electrode. Subsequently, seven Raman spectra of meat were obtained from the freshly cut surface of the SM muscle. For the Raman measurements, the mobile system as described in [9] was used. The integration time per spectrum was set to 2.5 s and six spectra were accumulated at each spot. For further analysis, all Raman spectra of each muscle were averaged.

After 24 h, the SM muscles were excised. During the deboning process, 15 samples were lost reducing the number of samples for subsequent analyses to 136. In the laboratory, two replicate pH measurements (pH_{24}) were conducted with a puncture electrode. Then, a 2.5 cm slice of the muscle was weighed, suspended in a box and stored for 48 h. After 3 d, the slices were reweighed and the difference between initial and ultimate weight was expressed as percentage drip loss.

Prediction models for the quality traits were calculated using partial least squares regression, PLS toolbox and MATLAB software.

III. RESULTS AND DISCUSSION

An overview of the results of the reference measurements is given in Table 1. The pH measurements in the abattoir were performed on average ten minutes earlier than the usual pH_{45} measurement, which partly explains the high mean pH of 6.58. The variation in the pH_{35} data as indicated by the standard deviation (SD) of 0.14 pH-units is rather small compared to the within-sample SD of 0.08 (Ref. Error in Table 1) which leads to a low ratio of SD/Ref. error of 1.8 for the pH_{35}.

The pH_{24} values scattered around a mean value of 5.42 with a standard deviation of 0.06. In contrast to the early postmortem pH, the reference error is only 0.02 pH-units, hence the ratio SD/Ref. error of 3.0 indicates a sufficient variance in the pH_{24} data set.

The average drip loss in this data set was 2.8 %. With a maximum value of 5.1 %, the data set contained only one sample with a drip loss above 5 %. Correspondingly, the standard deviation was low. As the drip loss measurement was conducted only once per sample, the reference error of 0.3-1.3 % was estimated from the literature [10]. Due to the margin of 1 %, the ratio SD/Ref. error ranges from 0.7 to 3.0.

Table 1. Overview of measured pH_{35}, pH_{24} and drip loss data and figures of merit for the PLSR models

	pH_{35}	pH_{24}	Drip Loss / %
Mean	6.58	5.42	2.8
SD	0.14	0.06	0.9
Min	6.09	5.30	0.9
Max	6.94	5.65	5.1
Samples	151	136	136
Ref. error	0.08	0.02	0.3-1.3*
R^2	0.75	0.58	0.83
RMSEC	0.07	0.04	0.4
R^2_{cv}	0.55	0.31	0.52
RMSECV	0.09	0.05	0.6

* from [10]

In summary, this data set comprises meat samples of high meat quality as indicated by high pH_{35}, normal pH_{24} and low DL. No deviating samples such as PSE or DFD were found in this random sample.

The Raman spectra were correlated with the pH and DL values using PLSR. The figures of merit of the correlations with the corresponding parameters are presented in Table 1.

The PLSR correlation of the Raman spectra and the pH_{35} values yielded good coefficients of determination with R^2=0.75 and R^2_{cv}=0.55. In Fig. 1, the pH_{35} values calculated from the Raman spectra are plotted against the measured pH_{35} values. Excellent RMSEC and RMSECV were calculated with 0.07 and 0.09 pH-units which are both in the range of the error of the puncture electrode (0.08 pH-units). In principle, the reference error is limiting the predictive ability of the regression model. In comparison to the earlier study [9], the prediction of the early postmortem pH was improved from RMSEC=0.11 to 0.07 pH-units and from RMSECV=0.17 to 0.09 pH-units. This improvement compared to the first study may be attributed to a number of reasons:

(i) a more than four times higher integration time per sample (105 *versus* 25 s) which is improving the signal-to-noise ratio by a factor two,

(ii) a shorter offset between pH and Raman measurement (5-15 *versus* 15-75 min),

(iii) a 50 % shorter period in which the Raman measurements were conducted (30 *versus* 60 min) and

(iv) a larger number of pH measurements per muscle (up to 6 *versus* 2).

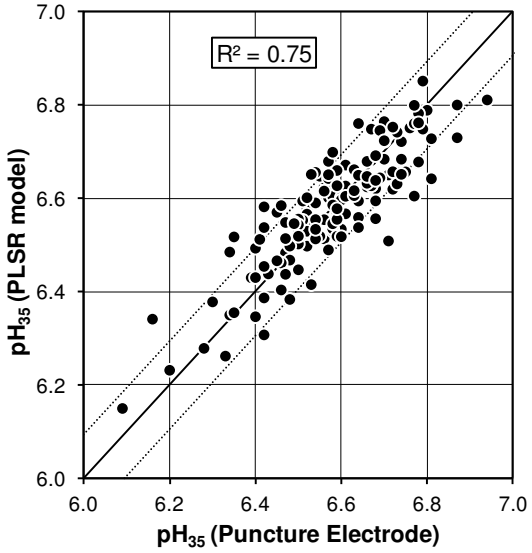

Figure 1. Predicted pH_{35} from Raman data 30-60 min p.m. using PLSR *vs.* pH_{35} measured with pH puncture electrode and RMSECV (dotted line)

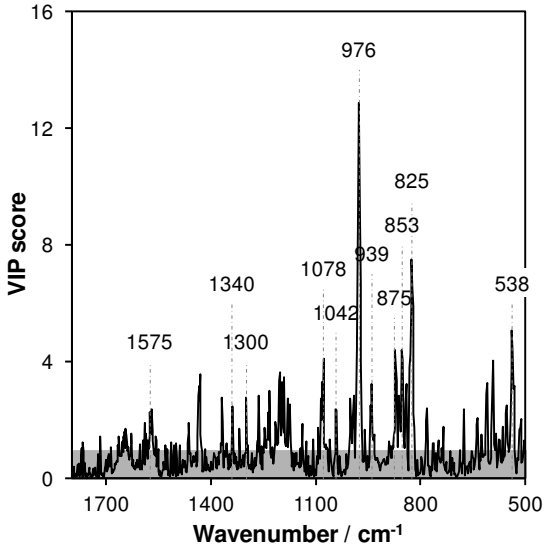

Figure 2. VIP plot of the PLSR model for the prediction of pH_{35} with peak assignments

Variable importance in projection (VIP) plots were used to determine Raman signals being relevant for the prediction of the reference parameter. In case of pH_{35} (see Fig. 2), the VIP plot reveals a strong influence of the phosphate vibration at 976 cm^{-1} and the associated vibration at 1078 cm^{-1} (for peak assignment, see [8]). Peaks at 538, 853 and 1042 cm^{-1} are assigned to lactate, while the peaks at 939 and 1340 cm^{-1} are related to glycogen. The signal at 1042 cm^{-1} in the Raman spectra is partly explained by a small contribution of sugar phosphates, but mostly by creatine, which has a second strong signal at 825 cm^{-1}. The signal at 825 cm^{-1} is weighted as the second strongest signal in the VIP plot indicating the influence of the creatine concentration for the pH_{35} model. This is explained by the high conversion rate of phosphocreatine to creatine in the time frame from 30 to 60 min [11]. Signals of phosphocreatine can be found at 849 and 978 cm^{-1}. The first is superimposed by the strong lactate vibration at 855 cm^{-1}. The partial cancellation of these signals may be the reason for the rather weak VIP score at 853 cm^{-1}. The latter adds intensity to the phosphate signal at 976 cm^{-1}. Besides the small VIP scores at 1300 and 1575 cm^{-1}, no indication for an influence of the ATP concentration can be found in this VIP plot. In conclusion, Raman peaks indicating the current metabolic state are used in combination with the pH-dependent signals of phosphate to calculate the pH_{35} from the spectra.

The previous study [9] has shown that this information can be utilized to predict six quality traits of which, to date, some can only be measured hours or even days after slaughtering. Hence, the spectra were also correlated with pH_{24} and DL.

The PLSR model for the prediction of pH_{24} yields R^2=0.58 and R^2_{cv}=0.31. This is rather poor in comparison to the results of the earlier study [9]. However, this is partly explained by the more than two times smaller standard deviation in the new data set. The PLSR model yields RMSEC=0.04 and RMSECV=0.05 pH-units, which are better compared to the earlier study (RMSEC=0.06, RMSECV=0.09 pH-units). The improved performance can be explained by the higher integration time, the shorter time frame in which the spectra were measured and the smaller reference error of the pH_{24} measurement in this field study.

Again, the VIP plot was used to reveal the most relevant Raman peaks for the pH_{24} prediction (not shown). This model mainly relies on the ATP concentration indicated by a peak at 1124 cm^{-1} and two additional ATP signals Furthermore, signals of lactate, glycogen and inorganic phosphate are weighted by the model.

The PLSR model for the prediction of drip loss yielded R^2=0.83 and R^2_{cv}=0.52. Due to the small variance of the DL data (SD=0.9 %), the coefficients of determination are rather low in this model. However, with RMSEC=0.4 % and RMSECV=0.6 %, its predictive power is

considerably higher than in the earlier study [9].
The VIP plot reveals strong influence of the phosphate concentration and the current pH value with the two phosphate signals at 976 and 1080 cm^{-1}. Besides, signals of lactate, creatine, phosphorylated sugars and ATP are weighted in the PLSR model.

IV. CONCLUSION

In this study, the non-invasive assessment of pH_{35}, pH_{24} and drip loss was shown by using a mobile Raman sensor early at the slaughter line of a commercial abattoir in the time frame from 30 to 60 min after slaughter. Promising prediction models with cross-validated errors in the range of the errors of the reference methods were derived from the Raman spectra. In comparison to a previous study, a significant improvement of the prediction errors (RMSECVs) was achieved amongst other by shorter time slots of the Raman measurements and a shorter delay between pH and Raman measurement. This is underpinning the potential of Raman spectroscopy for an accurate, non-invasive and early quality assessment of porcine muscles in intact carcasses. This could be of interest for an automatable sorting of the carcasses in parallel to the slaughtering process.

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