POST-RIGOR ASSESSMENT OF PORCINE MEAT QUALITY APPLYING A PORTABLE RAMAN SYSTEM

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Abstract – This contribution presents new results for the non-invasive quality assessment of pork using a prototype handheld Raman device. Earlier work has shown that pH_{45}, pH_{24} and drip loss can be predicted 0.5-2 h after slaughter with this device. Likewise, it is of interest to evaluate the potential of Raman spectra measured *post rigor*. Therefore, Raman spectra, pH values, color, drip loss and cooking loss of 137 porcine *longissimus thoracis* muscles were measured. The spectra correlated well with the pH_{24} (R^2_{cv}=0.7 and 0.82, for puncture and surface electrode, respectively) and L* (R^2_{cv}=0.67). The correlations with cooking loss 3 and 7 days p.m. and with drip loss were less precise (R^2_{cv}=0.33, 0.41 and 0.29, respectively). Thus, mobile Raman spectroscopy can measure important technological quality traits during deboning, but the predictive power is reduced compared to using pre-rigor spectra.

Key Words – pH, color, drip loss, PLSR

I. INTRODUCTION

The potential of Raman spectroscopy to predict important quality traits of porcine *semi-membranosus* muscles such as pH_{24} or drip loss (DL) from early postmortem spectra was already shown in the laboratory [1] and in commercial abattoirs [2]-[4]. This prediction of quality traits which are usually measured one or more days after slaughter is possible as the Raman spectra contain a variety of signals of important energy metabolites such as lactate, creatine phosphate and adenosine triphosphate [5] which are known indicators of the metabolic status of the muscle and of the resultant meat quality [6].
Previous studies with post-rigor pork revealed some potential to predict sensory quality traits [7], shear force (SF) and cooking loss (CL) [8]. Therefore, this study aims at exploring the potential of Raman spectroscopy to predict the quality traits pH_{24}, L*-value (luminosity), DL and CL of porcine *longissimus thoracis* (LT) muscles from spectra measured 24 h *post mortem* (p.m.).

II. MATERIALS AND METHODS

From a commercial meat processing plant in Switzerland, 137 pork carcasses of different origin (mostly Large White and Suisse Landrace crossbred) were randomly selected. At day one *post mortem*, the LT muscle was dissected and then used for Raman and reference measurements.
Raman measurements were conducted 24 h p.m. with a portable Raman device [3][9]. The laser power was set to 80 mW, the integration time was 2.5 s and 6 spectra were accumulated at each spot of a freshly cut meat surface. The Raman spectra from 7 spots per muscle were averaged for data analysis.
Two pH measurements were conducted per muscle with a puncture electrode and with a surface electrode, respectively. Then, two L* measurements were performed with a Minolta Chromameter. The drip loss was determined as percentage weight loss between day 1 and day 3 p.m. by measuring initial and ultimate weight of 2.5 cm slices of LT which were stored at 4°C freely hanging in a container. Cooking loss was measured at day 3 in the slice used for DL measurement and an additional 2.5 cm slice aged until day 7 p.m. The meat samples were weighed, vacuum-packaged, cooked in a water bath at 72°C for 45 min, unpacked, patted dry and weighed again. CL was calculated as percentage difference of initial and ultimate weight.
If applicable, the error of the reference method (Ref. error) was calculated from the averaged standard deviation divided by the square root of the repetitions per sample. It is noteworthy, that this calculation underestimates the error of the reference method in case of a small number of

Table 1: Results of the reference measurements of pH_{24} (PE = puncture electrode, SE = surface electrode), L*, drip loss (DL) and cooking loss (CL).

Parameter	pH_{24}		L*	DL	CL	
	PE	SE			3d	7d
N	137	137	137	137	137	136
Repetitions per sample	2	2	2-3	1	1	1
Mean	5.37	5.56	51.2	3.7%	29.7%	29.6%
Min	5.19	5.38	46.9	1.4%	23.3%	24.5%
Max	5.54	5.76	56.9	6.1%	34.7%	35.5%
σ	0.06	0.07	2.1	1.1%	2.1%	2.0%
Error of the reference	0.01	0.01	0.6	0.3-1.3%*	-	-
σ/Ref. error	5.5	5.3	3.5	0.8-3.7	-	-

* from [10]

repetitions. For DL, the error was taken from the literature [10].

Partial least squares regressions (PLSR) were calculated using the averaged Raman spectra and reference values of each muscle sample with MATLAB 7.9.0 R2009b (The Mathworks Inc., Natick, MA, USA) and the PLS Toolbox 7.5 (Eigenvector Research Inc., Wenatchee, WA, USA). Besides mean-centering, no further preprocessing was applied to the Raman spectra. The "random blocks" method was employed to cross-validate the models. The model's predictive power was improved by discarding spectral channels carrying little or no information relevant for predicting a particular quality trait. This method was described in detail earlier [3].

III. RESULTS AND DISCUSSION

An overview of the results of the reference measurements is given in Table 1.

The pH_{24} measured with the puncture electrode is low with an average of 5.37 pH-units and reveals little variation with σ=0.06 pH-units. The surface pH_{24} is 0.19 pH-units higher on average and reveals a similar variation of σ=0.07 pH-units. Interestingly, both pH_{24} values show a systematic discrepancy between each other and they are only moderately correlated with R^2=0.33. In both cases, the error of the pH measurement is very low with 0.01 pH-units. The ratio of variation within the pH_{24} values to the error of the reference method (σ/Ref. error) is 5.5 and 5.3 for the puncture and the surface electrode, respectively. This ratio is a good indicator for the suitability of a data set for chemometric modeling with methods such as PLSR. In general, a ratio above 2 is considered as sufficient [11].

The mean L*, DL, and CL values are corresponding to values found for normal or RFN (reddish, firm, non-exudative) pork. The ratio *σ/Ref. error* is 3.5 for L* and 0.8-3.7 for DL indicating good preconditions for PLSR modeling for L*. For DL, the margin is too high for a clear statement. As CL was determined only in one slice per ageing treatment and values for the error of this method could not be found in the literature, the ratio *σ/Ref. error* is unknown for CL. However, it was reported that CL can be determined with a repetitive precision of ρ=0.69, i.e. an acceptable reproducibility [12].

To evaluate to what extent the Raman spectra can be used to predict the aforementioned quality traits, PLSR models were calculated. Fig. 1 shows the result of the PLSR correlation of the Raman spectra with the pH_{24} values measured with the surface electrode. The figures of merit as presented in Table 2 confirm that the pH value can be very accurately determined from Raman spectra. Although the overall range of the pH values amounts to only 0.35 and 0.38 pH-units for the puncture or the surface measurement, reasonable correlations were found. The results even outperform former results with early postmortem spectra [3][4]. This can be explained by the much smaller variance within the pH_{24} values compared to pre-rigor pH values [1]. Moreover, the location where Raman and pH measurements were taken are closer together when a surface electrode is used instead of a puncture electrode, i.e. it is more

Table 2: Overview of figures of merit of the PLSR correlations between the Raman spectra and the reference values pH_{24} (PE = puncture electrode, SE = surface electrode), L*, drip loss (DL) and cooking loss (CL).

Parameter	pH_{24}		L*	DL	CL	
	PE	SE			3d	7d
R^2	0.89	0.96	0.92	0.40	0.51	0.62
RMSEC	0.020	0.014	0.6	0.9%	1.3%	1.3%
R^2_{cv}	0.70	0.82	0.67	0.29	0.33	0.41
RMSECV	0.032	0.031	1.2	0.9%	1.6%	1.6%

likely to measure spectra and pH at comparable positions.

In the VIP plot shown in Fig. 2, the Raman signal at 877 cm^{-1} assigned to inorganic phosphate is weighted as the most important peak [5]. The corresponding signals of the phosphate moiety at 978 and 1086 cm^{-1} are less pronounced as the pH_{24} differs only in the range from 5.38 to 5.56 in which the phosphate group is a relatively insensitive indicator for pH [1]. Hence, signals of other metabolites are also weighted such as glycogen (489, 1332 cm^{-1}), lactate (846 cm^{-1}), creatine (822, 1043 cm^{-1}) and phenylalanine (997 cm^{-1}) [5].

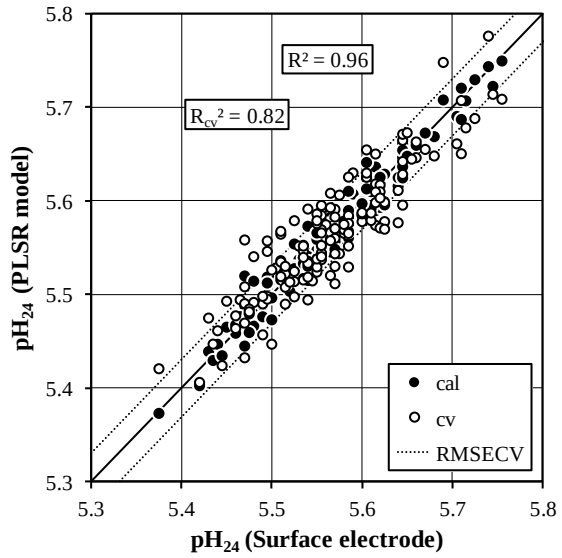

Figure 1. PLSR predictions of the pH_{24} measured with a surface pH electrode from calibration (cal) and cross-validation (cv).

The correlation of Raman spectra and L* also yields promising results with R^2_{cv}=0.67 and RMSECV=1.2. The latter equals 57% of the standard deviation within the L* data and is twice as high as the error of the reference method. These results confirm unpublished results of a series with 156 pigs. Hence, the luminosity L* as part of the meat color is likely to be predictable from post-rigor Raman spectra.

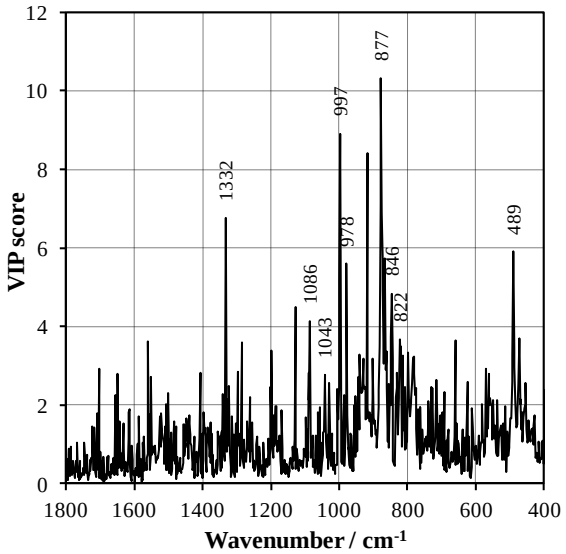

Figure 2. VIP scores of the PLSR model for the prediction of pH_{24} measured with a surface electrode. Selected signals marked by their wavenumbers.

The DL is less accurately predicted from the post-rigor Raman spectra (R^2_{cv}=0.29, RMSECV=0.9%). As the small variation of 1.1% within the DL data indicates (see Table 1), the undesired qualities PSE (pale, soft, exudative) and DFD (dark, firm, dry) were completely absent in this data set. Furthermore, considering the margin of error of the reference method (0.3-1.3%), this result could be explained by the statistical quality of the reference data. It is noteworthy, that DL was more accurately predicted from early postmortem Raman spectra in earlier studies [2]-[4]. This is due to signals assigned to compounds indicating the velocity of the energy metabolism of the muscle cells which is known to influence the DL.

This information is missing in post-rigor Raman spectra. Hence, the predictions have to rely on indirect effects such as the damaged muscle structure which alters the meat's scattering properties. Therefore, the post-rigor predictions are thought to be less accurate.
Likewise, only slightly better results were achieved for CL with R^2_{cv}=0.33 for CL_{3d} and 0.41 for CL_{7d} and RMSECV=1.6% for both models. This error is higher than in an earlier study (1.3%) [8]. However, the standard deviation within the CL data was 3.1% and therefore, the preconditions for PLSR modeling were better in the earlier study.

IV. CONCLUSION

In this study, post-rigor Raman spectra were shown to non-invasively measure and predict technologically relevant quality traits. The Raman spectra allow for an accurate determination of pH_{24} and L*-value. On the other hand, the correlation of the post-rigor Raman spectra with cooking loss and drip loss is moderate or rather low. Compared to the results achieved with pre-rigor Raman spectra [2]-[4], post-rigor spectra offer limited information about meat quality as most metabolic processes have come to a halt during *rigor mortis*. While pH_{45}, pH_{24}, drip loss (and possibly L*, b* and shear force) can be reasonably predicted from pre-rigor Raman spectra, post-rigor Raman spectra only accurately measure pH_{24} and L*, while prediction of DL and CL are poorer.

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