HAND-HELD RAMAN SYSTEM FOR AN EARLY POSTMORTEM DETECTION OF PH AND DRIP LOSS OF PORK MEAT

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Abstract – A portable Raman system was tested as a rapid and non-invasive optical device to determine the pH_{45} and to predict the pH_{24} and drip loss of pork meat using Raman spectra measured 1-2 h postmortem in a commercial abattoir. To this end, Raman spectra, pH_{45}, pH_{24} and drip loss were measured on the *semimembranosus* muscles of 96 pigs. The Raman spectra were correlated with pH and drip loss using PLS regression analysis. The pH_{45} was predicted with a coefficient of determination of $R^2 = 0.82$ and a standard error of cross validation RMSECV = 0.17 pH units. This model allows for a discrimination of PSE samples according to the pH<5.8 criterion with an accuracy of 98%. The correlations with pH_{24} yielded $R^2 = 0.84$ and RMSECV = 0.09 pH units, and with drip loss $R^2 = 0.90$ and RMSECV = 1.0%. These field results demonstrate that the handheld Raman system is suitable for Raman measurements in an abattoir 1-2 hours p.m. and that the spectra can predict the quality traits pH_{45}, pH_{24} and drip loss. Thus, the Raman device shows excellent potential for detecting PSE deviation and increased drip loss.

Key Words – Drip loss, Handheld Raman, pH_{45}, PSE detection, Ultimate pH

I. INTRODUCTION

The detection of water-holding capacity (WHC) of meat early in the production-chain is of high interest because a reduced WHC is an issue for meat processors and may cause economic loss. It is well known that meat showing a rapid postmortem metabolism is prone to a reduced WHC [1]. Here, the extreme deviation PSE (pale soft, exudative) is well understood [2]. The temperature, lactate formation and pH fall can be used as indicators [3], for example the pH_{45} which is well correlated with the WHC [4]. A number of methods have been evaluated for the prediction of PSE deviation and WHC in the production process by non-invasive methods [5-9].

Recently, Raman spectroscopy was shown to detect the pH in pork meat early p.m. which is essentially based on signals of phosphate and lactate [10, 11].

Raman spectroscopy is an emerging technique providing direct information of the molecular composition with only minor interference from the water content. The effect is based on inelastic scattering of light leading to the excitation of molecular vibrations in the sample.

In this study, we report on the first use of a portable handheld Raman system to measure the Raman spectra of pork meat 1-2 h after slaughter in an abattoir and to correlate the Raman spectra with the pH_{45}, pH_{24} and drip loss (DL) measured as reference parameters so as to predict these quality traits.

II. MATERIALS AND METHODS

Raman and reference measurements were performed with the topside (*M. semimembranosus, SM*) from 96 pigs representing a random sample of German breeds. Raman spectra and pH_{45} were measured in the cooling house of a commercial abattoir, while pH_{24} and DL were determined in the laboratory.

Duplicate pH measurements were performed 45 min and 24 h p.m. using a puncture electrode (Portamess 913XpH, Knick, Berlin, Germany). In the time frame from 24 to 72 h p.m. the DL was measured on a size-standardized sample. To this end, the meat sample was suspended and stored in a container at 4°C. The difference between initial and final weight was determined and expressed as percentage weight loss.

After the pH measurement, Raman spectra were captured 1-2 h after exsanguination on a freshly

cut meat surface using the 671 nm hand-held Raman probe described earlier [12]. The laser power was set to 80 mW and the integration time to 2.5 s. With these settings, ten Raman measurements were performed at different sites of each SM. For further analysis, all meat spectra per sample were averaged.

Partial least square regression (PLSR) was performed using MATLAB 7.9.0 R2009b software (The Mathworks Inc., Natick, MA, USA) with the PLS toolbox 6.2 (Eigenvector Research Inc., Wenatchee, WA, USA). For cross-validation the random blocks method with 9 data splits and 20 iterations was applied. To improve the predictive power (i.e. minimize RMSECV) of the PLSR models, the number of spectral channels was iteratively reduced to exclude spectral regions carrying little or no spectral information for the prediction [13]. To this end, VIP (variance importance in projection) plots and a threshold value of 1 were applied [14]. Thus, once a PLSR model was calculated, the optimal number of latent variables was chosen and the corresponding VIP plot was calculated. Subsequently, spectral channels with VIP scores lower than 1 were excluded from the data set. With the reduced data set a further PLSR model was calculated. This was repeated until a global minimum of the RMSECV was achieved. In our data set, it took 1 to 3 iterations to reach the minima and the RMSECV values could be reduced by 10 to 35%.

III. RESULTS AND DISCUSSION

The pH_{45} of the samples varied from a 5.41 to 6.80 (Table 1) showing some variance which is required for establishing a correlation. When applying the criterion $pH_{45}<5.8$ six samples were classified as PSE. The pH_{24} scattered around a mean of 5.53 ± 0.15 but also contained extreme values with five samples above 5.8 and three samples above 6.0. The latter three samples were classified as DFD meat. A relatively high number (30%) of the samples revealed DL>5% with up to 9.2%. The errors of the reference method (ref. error) for pH_{45} and pH_{24} were obtained during a series of measurements in the laboratory in which the variation of pH were monitored in 3 pork samples of SM muscles in the period from 0.5 to 10 h p.m. This experiment is presented in detail in [11]. The error of the DL measurement could not be determined in this way and was taken from the literature where it was reported to be between 0.3 and 1.3% [15].

Table 1 Overview of measured pH_{45}, pH_{24} and drip loss data and figures of merit for the PLSR models

	pH_{45}	pH_{24}	drip loss / %
Mean	6.29	5.53	4.1
SD	0.29	0.15	1.9
Min	5.41	5.28	0.7
Max	6.80	6.13	9.2
samples	96	96	81
ref. error	0.06-0.14	0.04	0.3-1.3*
R^2	0.82	0.84	0.90
RMSEC	0.11	0.06	0.6
R^2_{cv}	0.65	0.68	0.73
RMSECV	0.17	0.09	1.0

* from [15]

A PLSR model was calculated and optimized using VIP plots. This model is presented in Fig. 1 illustrating the correlation of pH_{45} measured with a puncture electrode versus pH_{45} predicted using the the Raman spectra obtained in the abattoir early postmortem. The RMSECV is indicated by two dotted lines in Fig. 1 to 3.

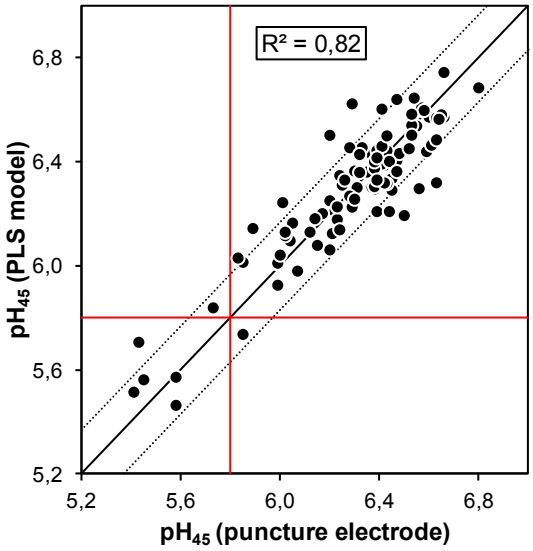

Figure 1. Predicted pH_{45} from Raman data 1-2 h p.m. using PLSR vs. pH_{45} measured with pH electrode

The coefficient of determination $R^2 = 0.82$ and $R^2_{cv} = 0.65$ are promising and the PLSR model yields RMSEC = 0.11 and RMSECV = 0.17 pH-units which are close to the estimated error of

the pH_{45} measurement of 0.06 – 0.14 pH units. Applying the PSE-criterion of pH_{45}<5.8, 94 out of 96 samples are grouped correctly with only two borderline samples being misclassified.

The PLSR model mainly relies on the Raman signal at 976 cm^{-1} which is mostly pronounced in the VIP plot (not shown). This signal is assigned to the basic form of the terminal phosphate group. The spectral region around 928 cm^{-1} and additional peaks at 1300, 1455 and 1644 cm^{-1} are weighted which point to α-helical protein signals [16, 17]. Two signals at 538 and 855 cm^{-1} can be assigned to lactate. The model utilizes further signals which match the spectral changes of Raman signals in pork meat early postmortem [11].

A second PLSR model was computed with the pH values measured 24 h p.m. In Fig. 2, PLSR predictions using the Raman spectra measured after 1-2 h are plotted versus pH_{24} values measured with a puncture electrode.

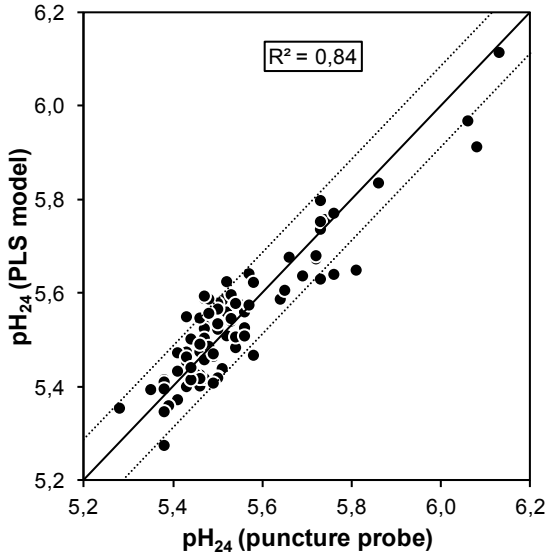

Figure 2. Predicted pH_{24} from Raman data 1-2 h p.m. using PLSR vs. pH_{24} measured with pH electrode

The model yields R^2 = 0.84 and R^2_{cv} = 0.68, and RMSEC = 0.06 and RMSECV = 0.09 pH-units. The prediction of pH_{24} is slightly better than the prediction of pH_{45}, which can partly be explained by the smaller variance of the ultimate pH value in pork meat [11, 15].

Interestingly, the three DFD samples with pH>6.0 are clearly separated (up right in Fig. 2) from the other samples. However, if with this criterion is applied to the Raman prediction this would lead to a misclassification of two of these samples. Nevertheless, the Raman spectra after 1-2 h show potential to identify DFD meat, but as the prevalence of DFD is very low further samples should be measured to confirm this.

Apparently, the PLSR model utilizes information from the Raman spectra beyond the detection of phosphate and lactate such as signals from glycogen which is already depleted in the DFD samples.

In Fig. 3, the PLSR correlation is shown for the DL predicted from the Raman spectra after 1-2 h for the DL measured after 72 h p.m. with the classical reference measurement.

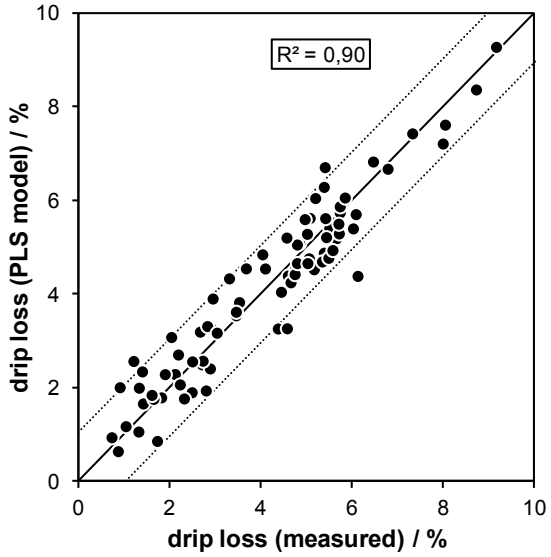

Figure 3. Predicted drip loss from Raman data 1-2 h p.m. using PLSR vs. drip loss measured with reference method

The model yields excellent results with R^2 = 0.9 and R^2_{cv} = 0.73, RMSEC = 0.6 and RMSECV = 1 %. Thus, the Raman spectra after 1-2 h can be used to accurately predict the DL which will occur three days later.

IV. CONCLUSION

A mobile Raman system for in-situ measurements of meat was tested in a field study under real-life conditions in the cooler of an abattoir with a

random sample of 96 pork carcasses. As reference parameters pH_{45}, pH_{24} and drip loss were measured. The PLSR correlations of the Raman spectra yielded very promising predictions for all of these three quality traits. Using VIP plots, the number of spectral channels was reduced and the prediction error was improved to the level of the error of the reference method.

These results confirm earlier laboratory experiments for the pH and lactate detection in excised SM samples.

Moreover, this study demonstrates the principal applicability of Raman spectroscopy to measure and to predict the three quality criteria pH_{45}, pH_{24} and drip loss with an early and non-invasive Raman measurement in the abattoir. Thus, in addition to the pH_{45} two further parameters can be acquired which are presently available only with additional efforts. Finally, the Raman spectra allowed for the detection of PSE meat and also showed potential for a DFD detection which could be useful for an early sorting of (the expected) meat quality.

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