CALIBRATION ROBUSTNESS IMPROVEMENTS FOR THE EARLY PREDICTION OF THE PH24 OF PORK WITH RAMAN SPECTROCOPY

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I. INTRODUCTION

The Raman spectroscopy ability to predict meat quality has been investigated for more than twenty years, and the early prediction of ultimate pH of pork meat is probably one of its most interesting feature, considering the expectations of French slaughterhouses about pork meat quality evaluation. A previous work has been performed on a French pork population at 30 minutes *post mortem* with a device dedicated to this purpose (671 nm emission laser spectrometer developed by H. Schmidt, Bayreuth University, Germany) [1] [2] and results were promising for both early prediction of ultimate pH (R^2_c=0.82) and drip loss (R^2_c=0.65). The 2018 dataset 2018 was large enough (n=206), but DFD samples (pH24 > 6.0; n=4) were too rare to build suitable models. The aim of this project is to select new samples with high pH24 values in order to improve the robustness of Raman prediction models based on spectra from deviated carcass. We also tested the ability of the Raman spectrometer to predict pH24 online, with a reduced integration time.

II. MATERIALS AND METHODS

Early *post mortem* carcass selection on ultimate pH value is challenging, and was applied according to the Vada-Kovacks protocol [3]. Carcasses were randomly deviated at 30 minutes *post mortem* in small batches (n=6) and a 3 g of the *Semimembranosus* muscle was collected and immediately minced in a 1.5% Triton X100 solution. Minced samples were incubated at 37 °C for 10 minutes, then the pH was measured. For each batch, 2 random carcasses got measured with the Raman spectrometer (15 s integration time and 7 repetitions), and the carcass with the highest Vada-Kovacks pH value was also selected for Raman measuring. In total, 550 carcasses were deviated and Raman spectroscopy was performed on 225 carcasses, of which 204 could be used for correlations. The reference meat quality parameters were recorded on the *Semimembranosus* muscle: early *post mortem* pH (30 min., pH1), ultimate pH at 24h *post mortem* (pH24), and drip loss on a 8 g sample of muscle after 48 h of storage at 6 °C (EZ protocol, [4]). Raman spectra were pre-processed with smoothing (Savitzky-Golay, window 7, order 1), EMSC (order 5), unit vector normalisation at 1000 cm^{-1} and mean centring. The pre-processed spectra were correlated with meat quality reference parameters with partial least-square regression using MATLAB 7.9.0 R2009b and Eigenvector PLS Toolbox 7.5. The number of latent variables (LV) was determined with venetian blinds cross validation procedure (10 data splits and 1 sample per blindness) as the lowest number of LVs providing a clear reduction of the rmsecv.

III. RESULTS AND DISCUSSION

Compared with the 2018 data set (n=206, [2]), the 204 new Raman spectra increased the DFD ratio from 1.9% to 9.3%, but did not improve decisively the pH24 variability (sd=0.20 *vs.* 0.17). To get a stronger impact of high pH samples, only the DFD and DFD tendency samples of this study (pH24>5.85; n=34) were added to the 2018 data set resulting in 22% DFD and DFD tendency samples in the augmented data set, n=240; table 1).

The models built with the augmented data set improved the robustness for the prediction of the pH1, pH24 and drip loss (R^2cv increase from +8%, +41% and +109% respectively, table 1) but calibration

errors (rmsec) rised also consequently. Cross-validation errors (rmsecv) remained stable and the Raman spectroscopy potential was confirmed with this second study.

Table 1 PLS regression results for the 2018 calibration (n=206) and the augmented data set (n= 240)

Parameter	n	LV	R^2 cal	R^2 cv	rmsec	rmsecv
pH_1	206	6	0.70	0.39	0.10	0.14
pH_{24}	206	7	0.82	0.44	0.07	0.12
Drip loss (%)	206	6	0.65	0.22	1.46	2.21
pH_1	240	7	0.57	0.42	0.12	0.14
pH_{24}	240	7	0.75	0.62	0.10	0.13
Drip loss (%)	240	7	0.59	0.46	1.80	2.10

Raman spectra obtained online with only 3 seconds of integration time (n=217) produced very weak linear prediction models for pH24 (R^2c=0.66 and R^2cv=0.04). However, pH24 sorting of carcasses at a 5.85 threshold value appeared feasible after PLSDA classification ($R^2c_{Matthew}$=0.99 and $R^2cv_{Matthew}$=0.34; results not shown).

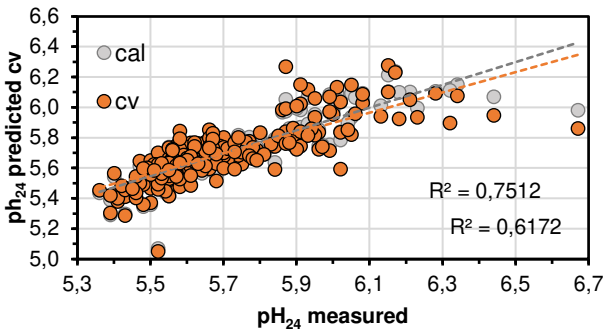

Figure 1. Prediction of pH24 with pre-rigor spectra (n = 240) for calibration (cal) and cross validation (cv)

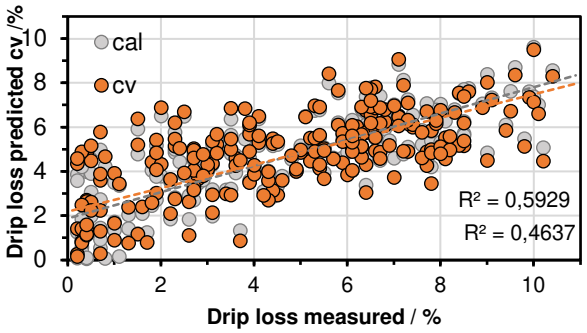

Figure 2. Prediction of drip loss with pre-rigor spectra (n = 240) for calibration (cal) and cross validation (cv)

IV. CONCLUSION

The updated determination coefficient of cross validation for the prediction of pH24 (R^2cv=0.62) and drip loss (R^2cv=0.46) showed a real potential for early *post mortem* carcass classification on their meat quality level. Compared to other technologies needing carcasses with stabilised pH at 24h *post mortem* (vision systems, NIRS), the Raman spectroscopy has the huge benefit to solve traceability problems due to its pre-rigor capability. However, further developments are needed in particular to reduce the measurement time, to plan validation tests on the slaughter line.

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