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# Evaluating the mineral nutrient status of fresh pasture herbage using laser-induced breakdown spectroscopy

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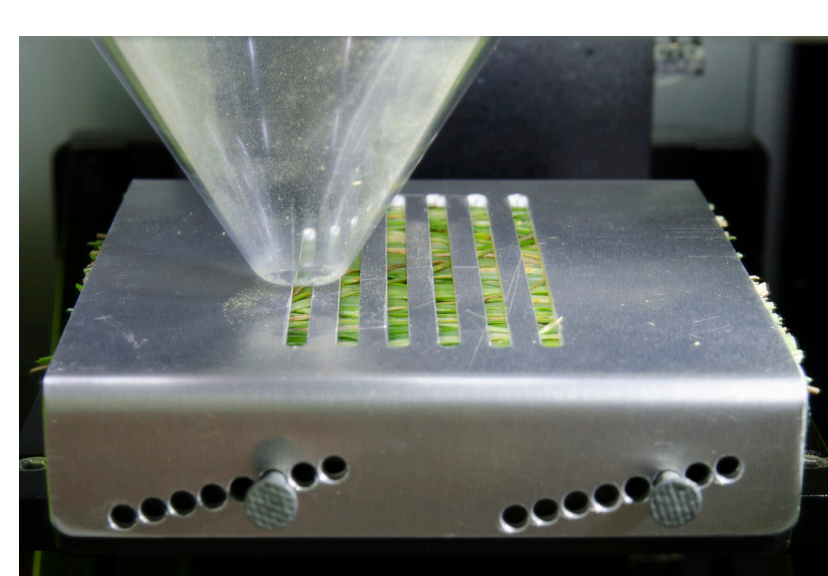
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## Background

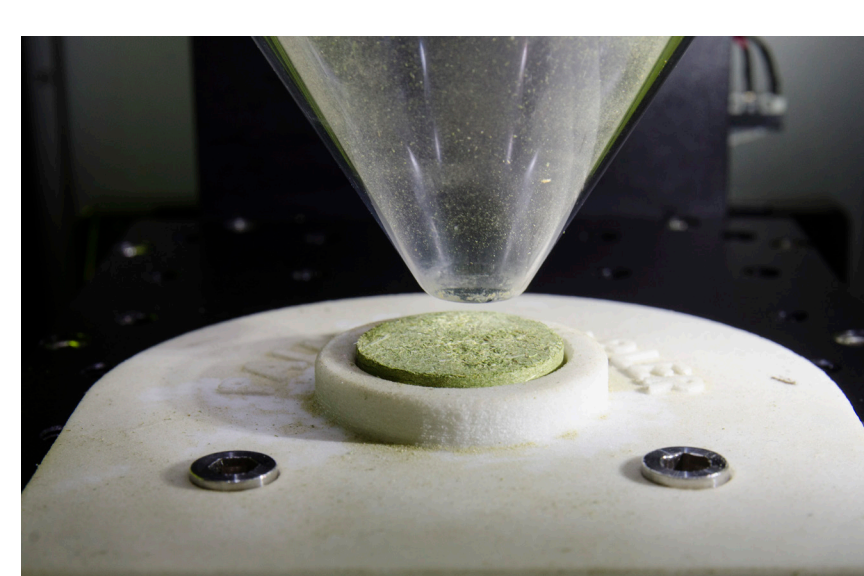
Precision agriculture is continually creating financial<sup>1</sup> and environmental benefits<sup>2</sup> through site-specific management of crops. However, there is currently no technology available for real-time, *in-situ* analysis of the mineral nutritional status of plants. Few measurement technologies have the required characteristics, such as (i) portability, (ii) high speed, (iii) specificity, (iv) sensitivity, (v) non-contact assessment, (vi) sample preparation, and (vii) simplicity<sup>3</sup>. Laser-induced breakdown spectroscopy (LIBS) has the potential to do so. If successful, LIBS-based technology could provide real-time information on the mineral nutrient status of plant material<sup>4</sup> and become an effective tool for precision agriculture.

## Methodology

- An Applied Photonics laboratory based LIBS-6™ system, housing a Q-switched Nd:YAG laser, operating at  $\lambda = 1064$  nm with pulse energy of 150 mJ (@ 6 ns) was used to obtain spectra of fresh ryegrass and ryegrass/clover mixed pasture over a 10-month period.
- 50-g samples were loaded into a holder which allowed a flat 'carpet' of individual leaves to be presented at a relatively uniform distance from the laser (Figure 1). Spectrum sets comprising of 100-shot accumulated spectra were obtained from each sample at a rate of 5 Hz.
- Following acquisition of LIBS spectra from the fresh pasture, samples were sent to a commercial laboratory for standard nutrient analysis, providing the elementary composition percentage by weight of dry matter of the most common elements (N, P, K, Na, S, Ca, Mg, Fe, Mn, Zn, Cu and B). Once standard nutrient analysis was completed, a second set of spectra was taken from pellets formed from compressed dried ground powder remaining after laboratory analysis (Figure 2).
- Calibration models predicting elemental nutrient concentrations from LIBS spectra were developed using 'black box' chemometric analysis. Spectra were pre-processed by using median filtering for baseline removal and mean centring in preparation for partial least squares (PLS) analysis. Between four and 14 latent variables were used with 10-way venetian blind cross-validation to form optimal calibration models.



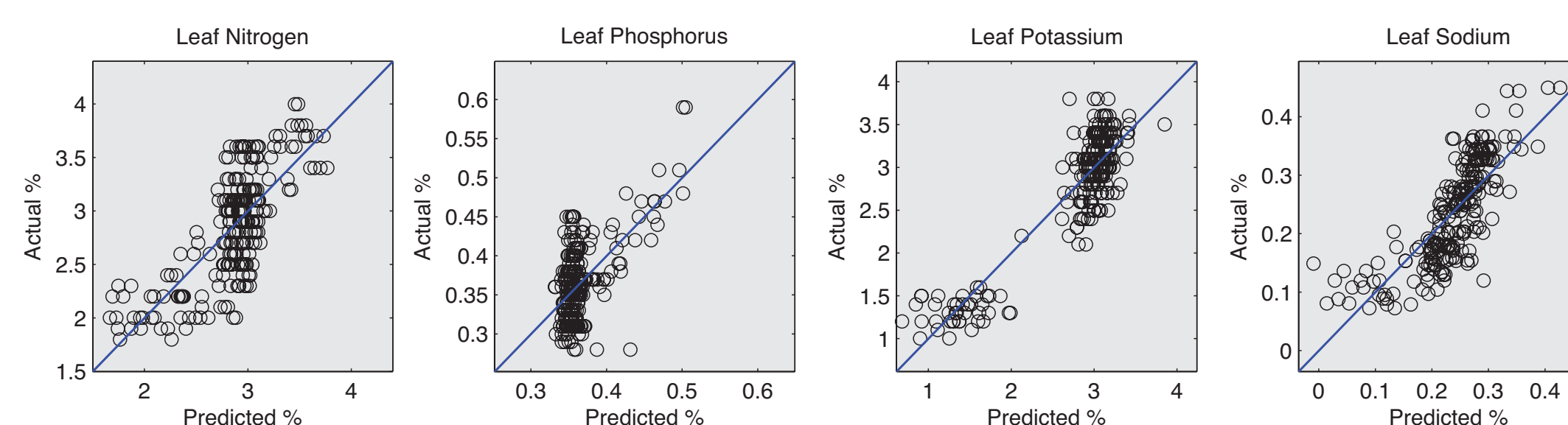
**Figure 1:** Sample holder containing samples of fresh ryegrass presented to the laser at a uniform height.



**Figure 2:** Sample holder containing samples of ground ryegrass in a pellet format exposed to the laser.

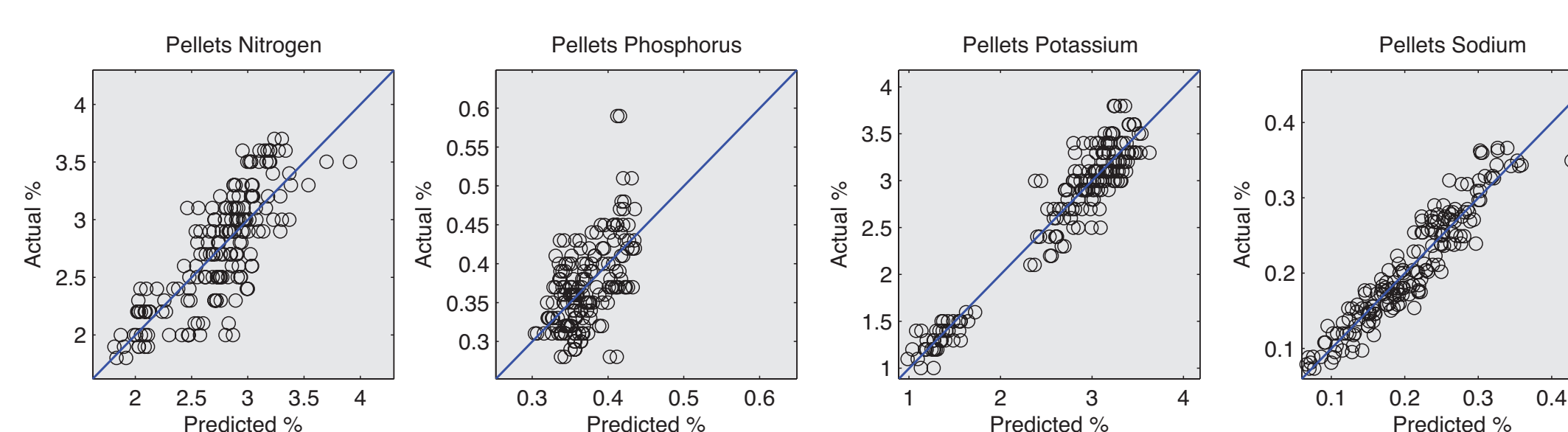
## Results

Results from the chemometric analysis have shown LIBS to be successful in identifying the mineral nutrient status of a number of plant elements. The more common elements, N, K, P and Na, are plotted for both fresh pasture (Figure 3) and pelletized pasture samples (Figure 4), with results showing the correlations between actual and predicted element concentrations. The pelletized samples led to more robust models, perhaps because of reduced energy loss in the water matrix.



Element	LV	R <sup>2</sup>	RMSEC	R <sup>2</sup> <sub>cv</sub>	RMSECV
Nitrogen	4	0.47	0.39	0.49	0.42
Phosphorus	5	0.41	0.04	0.29	0.06
Potassium	6	0.79	0.31	0.78	0.44
Sodium	8	0.72	0.04	0.48	0.08

**Figure 3:** N, K, P and Na calibrations statistics for predicting elemental concentrations from LIBS spectra of fresh pasture using PLS modelling with 10-way venetian blind validation, giving the number of latent variables used (LV), the correlation coefficients for calibration (R<sup>2</sup>) and validation (R<sup>2</sup><sub>cv</sub>) and the root mean square errors of calibration (RMSEC) and validation (RMSECV).



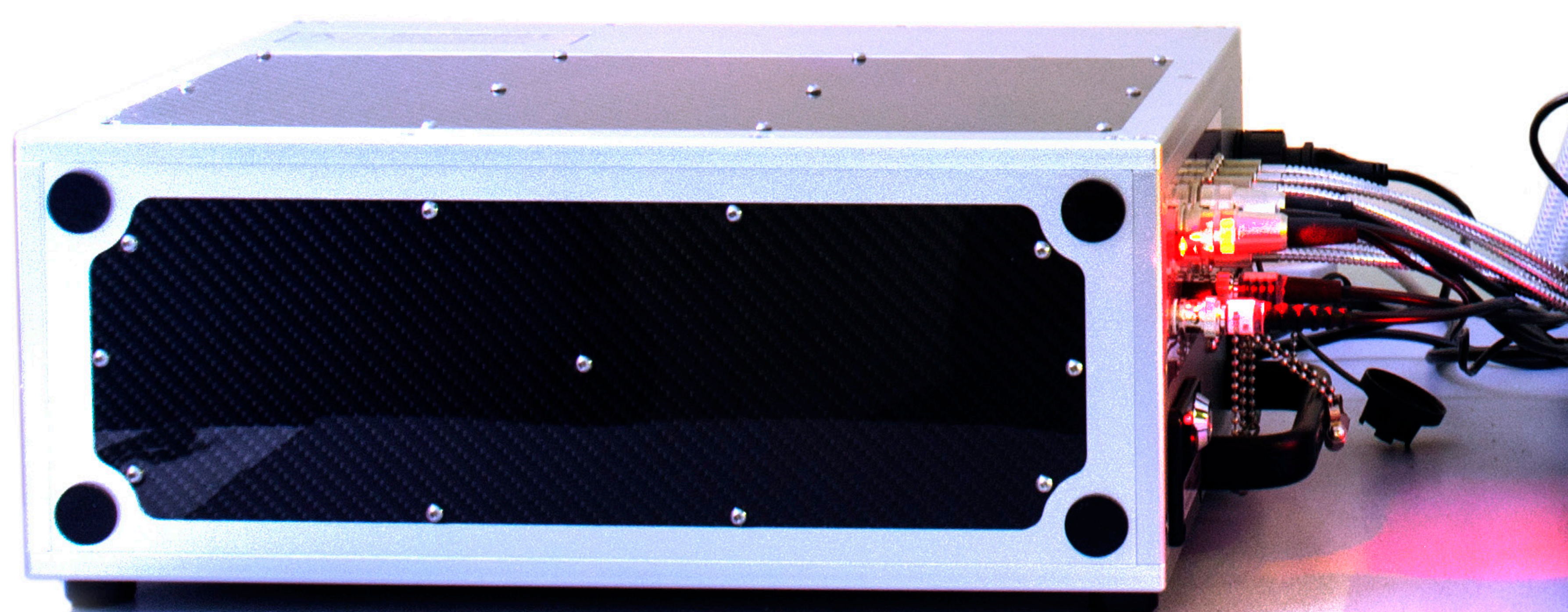
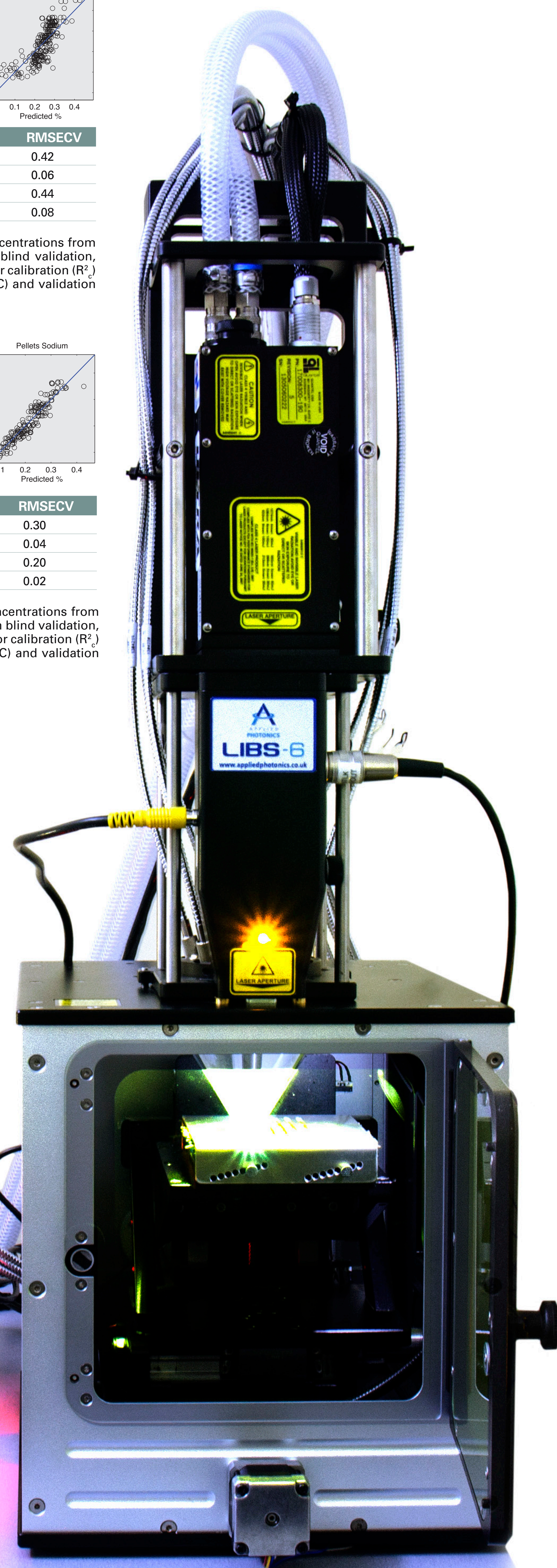
Element	LV	R <sup>2</sup>	RMSEC	R <sup>2</sup> <sub>cv</sub>	RMSECV
Nitrogen	4	0.73	0.27	0.65	0.30
Phosphorus	5	0.45	0.04	0.31	0.04
Potassium	6	0.95	0.17	0.94	0.20
Sodium	8	0.95	0.02	0.91	0.02

**Figure 4:** N, K, P and Na calibrations statistics for predicting elemental concentrations from LIBS spectra of pelletized pasture using PLS modelling with 10-way venetian blind validation, giving the number of latent variables used (LV), the correlation coefficients for calibration (R<sup>2</sup>) and validation (R<sup>2</sup><sub>cv</sub>) and the root mean square errors of calibration (RMSEC) and validation (RMSECV).

## Conclusion

We have shown that LIBS can identify a number of elements in fresh pasture using a simple chemometric approach. We believe LIBS has the ability to be an effective tool for precision agriculture, providing in-field, real time, mineral nutrient analysis on fresh pasture.

Further investigations into the calibration analysis are warranted. We hope further elements can be identified and results improved by performing rigorous emission spectroscopy analysis. Accuracy could be further improved by creating a tighter laser focus by using an auto focus mechanism or creating a better defined fixed object/laser distance.



## Acknowledgements

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## References

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