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Hydroponics Monitoring Through UV-Vis Spectroscopy and Artificial Intelligence: Quantification of Nitrogen, Phosphorous and Potassium†

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Abstract: In hydroponic cultivation, monitoring and quantification of nutrients is of paramount importance. Precision agriculture has an urgent need for measuring fertilization and plant nutrient uptake. Reliable, robust and accurate sensors for measuring Nitrogen (N), Phosphorus (P) and Potassium (K) are regarded as critical in this process. It is vital to understand nutrients' interference; thusly, a Hoagland fertilizer solution-based orthogonal experimental design was deployed. Concentration ranges were varied in a target analyte independent style: [N]= [103.17-554.85] ppm; [P]= [15.06-515.35] ppm; [K]= [113.78-516.45] ppm, by dilution from individual stock solutions. Quantitative results for N and K, and qualitative results for P were obtained.

Keywords: nitrogen; phosphorus; potassium; Hoagland; nutrient; spectrophotometry; interferences

1. Introduction

Fertilizer usage represents an important part of traditional agriculture and crop yield. In a world of growing food (and other agricultural products) demand – estimates indicate up to 50% increase in the 2012-2050 time frame [1] – fertilizer (ab)use is seldomly a goto solution for crop yield increase. Additionally, although growth rates for arable land are expected to increase within a sustainable manner, if an arable land loss scenario due to climate changing conditions is taken into account [2], further conflicts and competition might arise between protected lands, agricultural exploitation and human expansion.

Considering these concerns – well reflected by the United Nation's 2030 Agenda for Sustainable Development [3] – and also motivated to provide a solution for sustainable agriculture, our group has undertaken the task to develop a technology that is able to help farmers ensure that their crops' needs are being met, through their fertilization procedures. Knowing what is being fed to the crops and what is being uptake, it is possible to reduce water/fertilizer consumption to an optimal level, reducing the operational costs, whilst allowing crops to develop at their optimal speed, towards a bigger crop turnover.

Spectroscopy is, among others, one of the most well-established techniques for chemical identification and quantification. Several chemical determination methodologies that rely on spectroscopy exist (e.g., ICP-AES, LIBS, FTIR, GC-VUV); nevertheless, limitations also exist: the sample must be responsive to electromagnetic radiation (absorption/emission); linearity outside the Beer-Bouguer-Lambert Law [4–6] can sometimes be problematic, or the simple fact that spectroscopy is a molecular-level information tool, which can add entropy to the analysis by providing a wider range of information than the one desired. If pure compounds are analysed, little or no interference exists; when more complex mixtures are targeted, interferences might play a key role on the successful outcome. In such cases, in order to obtain an accurate and reliable measurement, interferences have to be taken into account. Chemometrics presents itself as a putative solution to, by employing varying complexity mathematical calculations, together with statistics and algorithms allow the extraction of relevant information from the superimposed and – sometimes – latent data. Linearity-based models are unable to solve the interference pattern between any constituents present: either interferents and non-interferents (target analytes), due to the fact that light has a wave-like nature and, hence the sample information might suffer from constructive or destructive interferences [7]. Nevertheless, new chemometrics methodologies that encompass interferences already allow critical developments to be achieved, *e.g.*, on health-related Point-of-Care analysis [8].

In hydroponics, most of these interferences can be attributed to the fertilizers. Fertilizers are mixtures of several different nutrients, mostly in their inorganic salt form (*e.g.*, $MgSO_4$, $CaCO_3$, $FeCl_3$) whilst some might be in aqueous solutions (*e.g.*, Mo, Ba, B). In complex mixtures, some signals might superimpose over others, causing a concentration misevaluation, or resulting in a continuous spectrum of overlapping signals.

This study aims to provide insight on the interferences within a complex matrix orthogonal design consisting of 8^3 independent concentration Hoagland solution samples. The performed assay further complements on our previous findings [9] on the feasibility of information extraction of highly constrained samples, by using an advanced algorithm – Self-Learning Artificial Intelligence (SLAI) – in order to find the adequate co-variance modes for accurate model prediction.

2. Materials and Methods

Hoagland solutions were chosen as a matrix due to their widely accepted status among the agronomical community as being a good model for complex nutrient solutions in hydroponics. Stock Hoagland solutions are composed as described by Table 1.

Table 1. Half strength Hoagland solution individual component concentration.

Element	Ionic Form	C (ppm)	C (mM)
	Macronutrients		
Potassium (K)	K^+	117.29	3.00
Calcium (Ca)	Ca^{2+}	80.16	2.00
Magnesium (Mg)	Mg^{2+}	24.31	1.00
Nitrogen (N)	Total N	105.06	7.50
	$N(NH_4^+)$	7.01	0.50
	$N(NO_3^-)$	98.05	7.00
Phosphorus (P)	Total P (HPO_4^{2-}; H_2PO^4) *	15.49	0.50
Sulfur (S)	SO_4^{2-}	32.08	1.00
	Micronutrients		
Chlorine (Cl)	Cl^-	0.324	9.15
Boron (B)	BO_3^{3-}	0.250	23.12
Manganese (Mn)	Mn^{2+}	0.251	4.57
Zinc (Zn)	Zn^{2+}	0.025	0.38
Copper (Cu)	Cu^{2+}	0.0102	0.16
Molybdenum (Mo)	MoO^{4-}	0.0053	0.06
Iron (Fe)	Fe^{2+}; Fe^{3+} **	2.500	44.77
Sodium (Na)	Na^+	1.029	44.77

The ratio of ionic forms depends on *the pH and **also on the O_2 level within the nutrient solution.

Three stock solutions for N, P and K were freshly and individually prepared in order to be possible to vary each target element (N, P or K) independently. Each stock solution comprised of ionic elements already present in the base matrix: N – $NaNO_3/NH_3$; P – H_3PO_4; K – KCl. The ratio of $NaNO_3/NH_3$ of the stock spiking solutions was the same as the ratio on the Hoagland solution (≈93:7).

Final concentrations of all samples (matrix + individual spikes) were corrected taking into account any variations derived from the preparation of fresh stock solutions each day during the execution of the assay.

The tested final concentration ranges, for the target analytes, were as described in Table 2.

Table 2. Tested concentration ranges for N, P and K within the design matrix.

	Concentration (ppm)			Concentration (mM)		
	N	**P**	**K**	**N**	**P**	**K**
Minimum	103.17	15.06	113.78	7.37	0.49	2.91
Maximum	554.85	515.35	516.45	39.61	16.64	13.21

The designed orthogonal matrix was composed by 8^3 samples, each one with an independent N, P and K concentration level. At each corresponding level, the N, P and K corresponding spike was added to the matrix and stirred for 10 s in order to attain full homogeneity. Afterwards, the pH value was registered (Crison GLP 21, Crison Instruments, SA – Barcelona, Spain) and the sample pumped into a custom-built flow cell for spectral data acquisition. Each sample had a final total volume of 30 mL (Hoagland + [N + P + K] spikes). After data acquisition, the sample was discarded and the system flushed with deionised water.

Data acquisition was performed with an in-house LabView-based developed software (National Instruments™ Corp. – Texas, USA) for pumping control and data acquisition.

Sample irradiation was performed with a D_2 light source (FiberLight® D_2 HighPower DTM 10/50S, Heraeus Noblelight GmbH – Hanau, Germany) whereas the detection was performed by a miniaturized spectrometer with a 190-650 nm range (STS-UV-L-50-400 Ocean Insight, Inc.). Individual components were assembled with custom-length 600 nm UV-Vis optical fibres, as depicted in Figure 1.

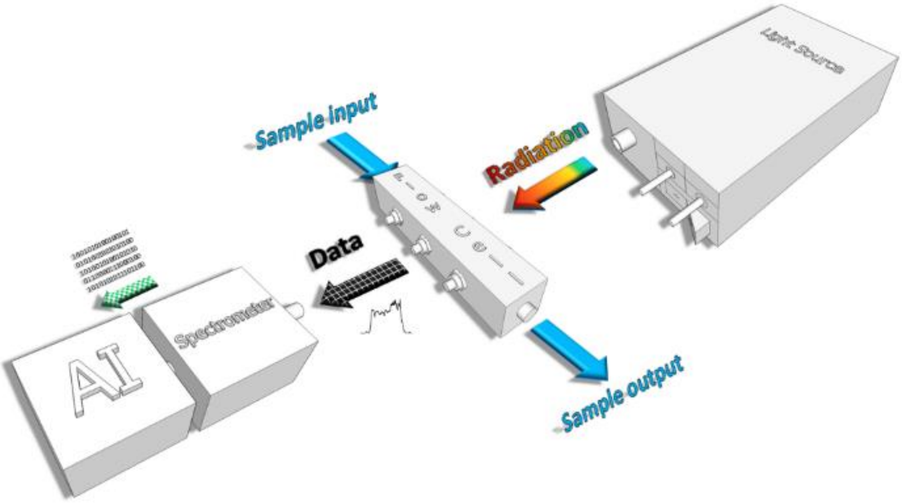
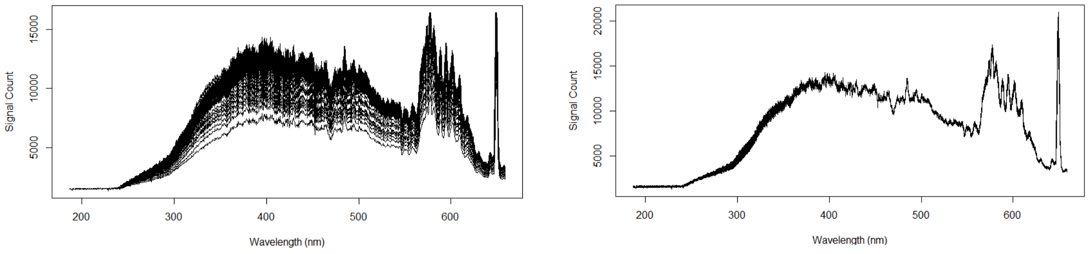


Figure 1. Scheme for individual components arrangement, within the developed prototype.

3. Results

The obtained results from the execution of this matrix were compiled and are depicted on Figure 2.

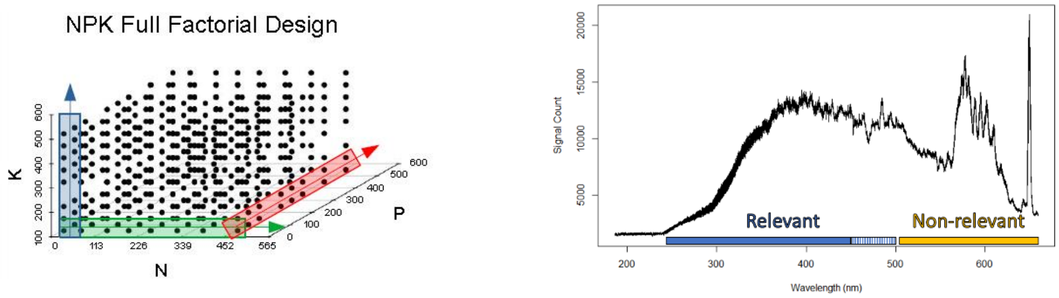
The collection of spectral data and cross correlation with the concentration information for each solution was performed. Spectroscopy signals were processed accordingly to [7]. Nevertheless, using advanced signal processing it is possible to train the system to recognize and extract the information from the relevant features, incorporating multi-scale interference into the NPK quantification models.



(**a**) (**b**)

Figure 2. Compiled spectra (8^3 samples) without (**a**) and with scatter correction (**b**).

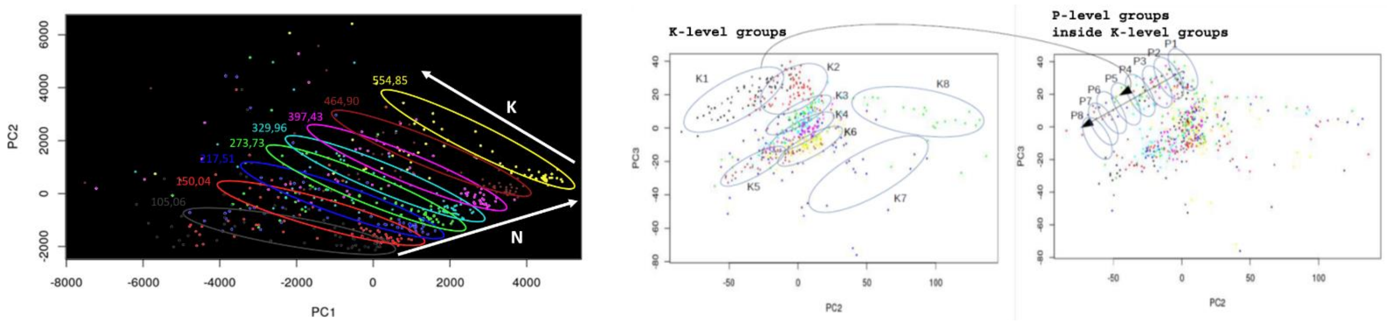
The correlation of the different levels among the NPK nutrients of the matrix design, can be represented as displayed by Figure 3 (**a**) whereas Figure 3 (**b**) shows the corresponding recorded spectra in the UV-Vis region (*circa* 200 - 650 nm) of the factorial design samples. As expected, most of the systematic spectral variation occurs at ≈250 to 450 nm, and, to a lesser extent, to 500 nm. This figure provides evidence that information about P and K is present, because, even to the naked eye, one can observe that there are more spectral patterns in the region of ≈250 to 450 nm than the expected nitrogen levels of the experimental design; that is a good indication that the interferences between all the constituents are being registered on the spectra.



(**a**) (**b**)

Figure 3. Sample distribution of the NPK full factorial design (**a**), whole matrix data (with scatter correction) of the relevant wavelengths of the obtained spectra, where most of the relevant NPK-bearing information is contained (**b**).

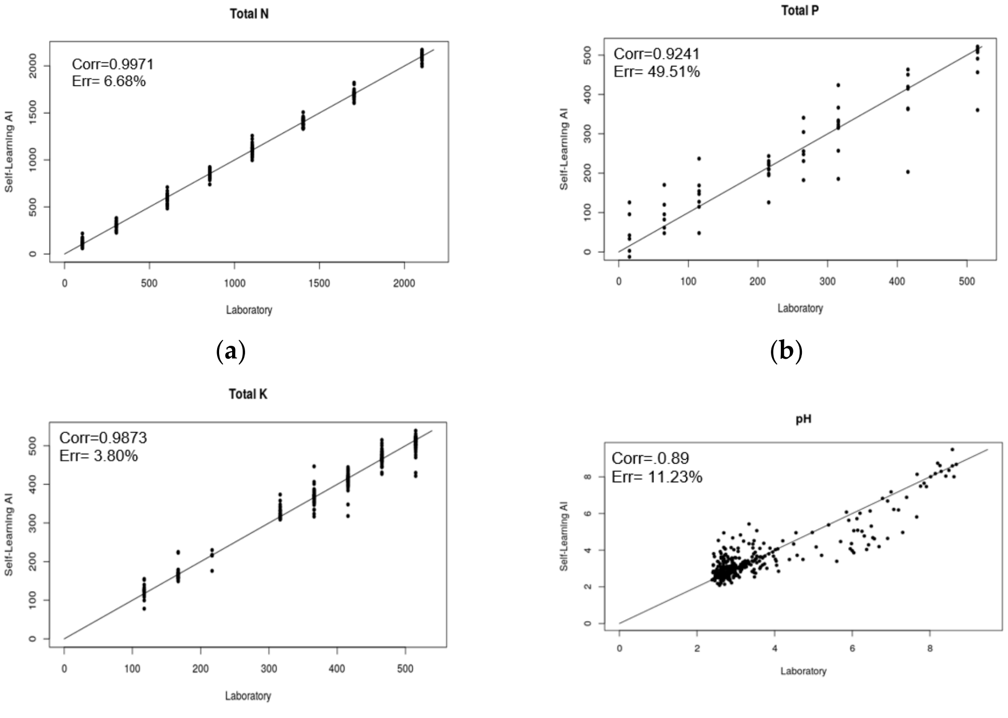
The Principal Component Analysis (PCA) (please refer to Figure 4 (**a**)) scores plot of the corresponding experimental design spectra are shown, where the different colours represent the different levels of total nitrogen. The main variance present in the spectra corresponds to the nitrogen absorbance, where the first principal component is highly correlated to the nitrogen content. It is also possible to see that the K-level information is embedded inside each N-concentration level. Analysis of the second component allows to unveil that information of K-level also carries the information of the different P-levels of the sample matrix (please refer to Figure 4 (**b**)).



(**a**) (**b**)

Figure 4. Principal components analysis (**a**) and the information of K-levels within the N-levels (**b, left-hand side**) whereas (**b, right-hand side**) demonstrates the information of P embedded within K-level groups.

Using the data obtained from the executed matrix, it was possible to train the Self-Learning AI of the system in order to quantify N and K with 6.7% (0.997) and 3.8% (0.987), respectively, and to obtain qualitative results for P, as shown in Figure 5.



(**a**) (**b**)

(**c**) (**d**)

Figure 5. Matrix results for total N (**a**), total P (**b**), total K (**c**) and also pH (**d**). Quantitative results for N and K, whereas qualitative results for P are possible to be inferred.

4. Conclusions

A NPK spectroscopy-based, AI-supported by a robust Self-Learning Artificial Intelligence was developed in order to be able to cope with increasing interference complexity of fertilizer solutions in greenhouses. The obtained results allow to be inferred that the current system's performance is adequate for Hoagland solutions, which are used in research and high-end hydroponic systems.

The assembled system aimed to keep a good balance between cost-benefit, without relinquishing reliability, robustness and accuracy; this objective has been successfully attained.

Further analysis of the results – not within the scope of this manuscript – as well as of unpublished data, allows further developments to be implemented to the system/prototype, in order to enhance its robustness and accuracy.

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Conflicts of Interest: The authors declare no conflict of interest.

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