



FINAL REPORT 2015

Applicants must read the *SAGIT Project Funding Guidelines 2014* prior to completing this form. These guidelines can be downloaded from www.sagit.com.au

Final reports must be emailed to admin@sagit.com.au as a Microsoft Word document in the format shown **within 2 months** after the completion of the Project Term.

PROJECT CODE	:	UA0313
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PROJECT TITLE	(10 words maximum)
XRF as a tool for measuring crop nutrient contents in the laboratory and the field	

PROJECT DURATION

*These dates **must** be the same as those stated in the Funding Agreement*

Project Start date	01/07/2013
Project End date	30/06/2015

PROJECT SUPERVISOR CONTACT DETAILS

The project supervisor is the person responsible for the overall project

Title:	First Name:	Surname:	
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Office Use Only

Project Code

Project Type	
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ADMINISTRATION CONTACT DETAILS

The Administration Contact is the person responsible for all administrative matters relating to the project

Title: Ms	First Name: Chelsea	Surname: DuBois	
Organisation: University of Adelaide			
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Telephone:	Facsimile:	Mobile:	Email:

PROJECT REPORT

Provide clear description of the following:

Executive Summary (200 words maximum)

A few paragraphs covering what was discovered, written in a manner that is easily understood and relevant to SA growers. A number of key dot points should be included which can be used in SAGIT communication programs

XRF has been shown to provide an accurate assessment of various nutrient concentrations (Ca, K, P, S and Zn) in prepared (dry, ground) plant samples of a wide range of crops applicable to S.A. broad acre agriculture.

XRF has also shown potential in estimating nutrient concentrations in various crop types in the field however at low concentrations of phosphorus, sensitivity and subsequent correlations with laboratory determination (acid digestion/ICP) were reduced. This can be attributed to water contents in leaf material reducing density and therefore reducing the signal detected by XRF.

Plant samples taken from the field and dried before XRF analysis improved performance significantly. Samples didn't need to be ground before XRF analysis.

Measurement of grain nutrient concentrations of intact grain heads proved difficult expect for Zn which showed excellent correlations with laboratory determination. Performance of XRF improved slightly when grain heads were threshed and analysis was performed on whole grains however overall XRF counts were reduced.

Excellent correlations were produced between XRF and laboratory determination of nutrient concentrations in subsequent ground grain samples.

Project Objectives

A concise statement of the aims of the project in outcome terms should be provided.

This project will assess the potential of hand held XRF technology for accurate and cheap analysis of important macro and micronutrients in samples in the laboratory and in plant tissue in situ in the field.

To fulfil the objective the project will aim to:

1) Determine the relationship between XRF and ICP values for P (plus other macro and micronutrients, Ca, Cu, K, Mn, S and Zn) contents on a range of crop vegetation and grain.

2) Describe the effect of different plant (tissue and grain) matrices on the relationship obtained in 1) and assess whether different calibrations are required depending on which crop type is being assessed.

3) Determine if samples for XRF analysis need to be prepared (dried and ground) before analysis which is a procedure required for ICP analysis and therefore determine the applicability of measuring P and nutrients for plant tissues in situ in the field.

Overall Performance

A concise statement indicating the extent to which the Project objectives were achieved, a list of personnel who participated in the Research Project including co-operators, and any difficulties encountered and the reasons for these difficulties.

Key Performance Indicators (KPI)

*Please indicate whether KPI's were achieved. The KPI's **must** be the same as those stated in the Application for Funding and a brief explanation provided as to how they were achieved or why they were not achieved.*

KPI	Achieved (Y/N)	If not achieved, please state reason.
Determine relationships between XRF and ICP for P (plus - Ca, Cu, K, Mn, S and Zn) on a range crop vegetation and grain.	Y	
Evaluate the potential of using XRF as an tool to determine in situ plant nutrient concentrations in the glasshouse	Y	
Evaluate the potential of using XRF as an tool to determine in situ plant nutrient concentrations in the field	Y	

Technical Information (Not to exceed three pages)

Provide sufficient data and short clear statements of outcomes.

Determine relationships between XRF and ICP for P (plus - Ca, Cu, K, Mn, S and Zn) on a range crop vegetation and grain.

Further information can be found in the 2013 progress report and accompanying supplement which contained all correlations.

From prepared (dried and ground) peak biomass samples taken from various locations in the field we have established calibration sets for the following crop types; canola, chickpea, field pea, lupin, rye, vetch and wheat (with a small amount of lentil samples). Correlations with ICP measurements for P, S, Ca, K and Zn with each crop type can be found in the 2013 progress report. Other elements for investigation in the project (Cu and Mn) fell below detection limits of the XRF for most samples. The XRF was run using an in built method (Mining Cu/Zn) and each sample was analysed for 2 minutes. From this data we can program in our calibration parameters so the instrument will display a correct unit of element analysed (e.g. one that matches an ICP measure). Excellent significant ($p \leq 0.01$) correlations were found for most crop types and elements. All relationships presented graphically can be found in the 2013 progress report.

Excellent significant ($p \leq 0.01$) correlations have also been produced for prepared grain samples. Importantly it appears the correlation parameters between dry matter and grain are very similar and an excellent overall calibration can be obtained when you combine the two (table 1) and using P as an

example (figure 1). Reduced correlations for S can be attributed to a very small range of S concentrations in both vegetative dry matter and grain.

Figure 1: Relationship between P concentrations in dry matter and grain of wheat determined by acid digestion followed by analysis with ICP and that determined by XRF.

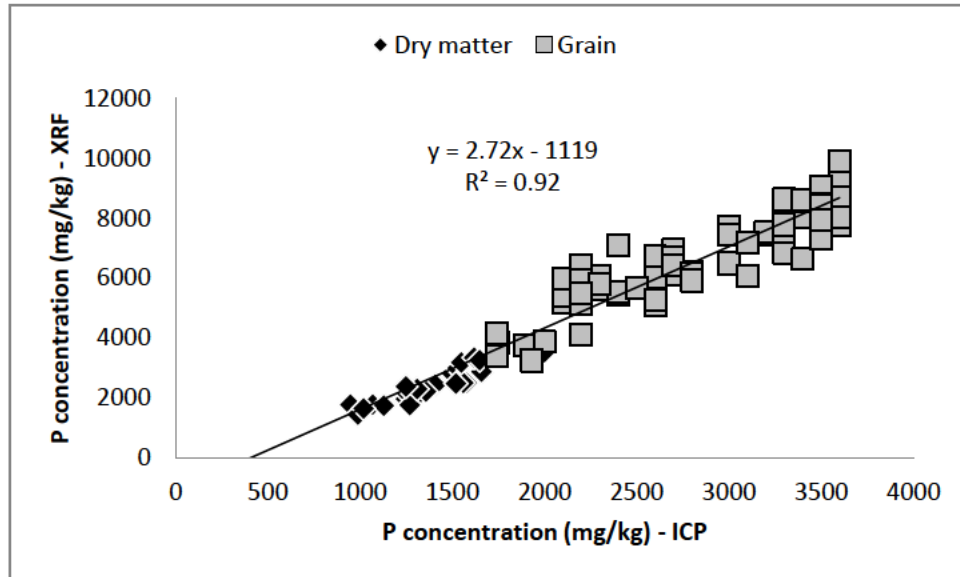


Table 1: Correlation parameters between nutrient concentrations measured by ICP and by XRF for grain samples only and combined with dry vegetative samples

	Grain (prepared)		Dry matter + grain	
	Slope (y)	Correlation (R ²)	Slope (y)	Correlation (R ²)
Phosphorus	2.4	0.81	2.72	0.92
Sulphur	4.65	0.29	3.17	0.38
Potassium	2.27	0.53	2.54	0.95
Calcium	3.14	0.64	2.23	0.97
Zinc	3.05	0.73	3.11	0.74

Evaluate the potential of using XRF as an tool to determine in situ plant nutrient concentrations in the glasshouse

First known evaluation of XRF as an in situ measurement of selected plant nutrients was performed by growing one plant of the following; field pea (kaspera), canola (snapper) and wheat (frame) in 24 different soils of varying nutrition in order to obtain a wide range of P (S, Ca, K and Zn) concentrations in the leaf. At the equivalent growth stage of mid tillering in wheat the youngest emerged blade of wheat and canola was cut and immediately analysed by XRF (fresh). For field pea the two leaves on the third branch were analysed. After XRF analysis samples were dried in an oven at 40°C. Samples were then analysed again by XRF (dried) followed by acid digestion and leaf nutrient concentrations determined by ICP-OES analysis.

Initial results for P indicate there is a moisture effect on the analysis of the leaf samples by XRF with lower correlation coefficients (R²) obtained for field pea and wheat with ICP results compared to high correlations obtained by leaf samples after drying. Generally lower relationships were obtained for Ca, K and S for both fresh and dried samples compared to P potentially due to an overall reduced distribution of values within each crop type for the soils used. Moderate relationships could be

obtained for Ca and S when all crop types were combined which increased the distribution of values. Relationships of P concentrations determined by XRF, both fresh and dried samples with ICP can be found in the 2013 progress report.

Evaluate the potential of using XRF as a tool to determine in situ plant nutrient concentrations in the field

In situ field analysis of leaf nutrient contents by XRF occurred at three main field sites utilising phosphorus responsive trials established through project UA1201 (wheat and barley) and also the Hart field site (canola, beans and field peas). Two of these sites (UA1201) provided varying concentrations of at least P in the plants due to the application of various rates of P (0, 5, 10, 25, 40 kg/ha). Wheat and barley samples at growth stages GS31—32 were analysed by XRF at both Condowie and Sherwood. The youngest fully emerged blade on the main stem was analysed in-situ with XRF for the first three rows of each trial providing 30 samples each of wheat and barley. Leaf samples were bagged and taken back to the laboratory where they were dried upon arrival. XRF analysis was again performed on intact samples. For half of the in-situ field analysis and all of the samples brought back to the laboratory, two different locations on the leaf (roughly one in the lower half and one in the upper half) were analysed by XRF to provide an assessment of the heterogeneity of P in particular in the leaf. Samples were then analysed for nutrient content by ICP-OES analysis after acid digestion of the samples. XRF values were compared to those obtained by ICP analysis.

All leaf samples (oldest to youngest) from two plants each of canola, bean and field pea were analysed by XRF both in the field and laboratory. These crops were in a more advanced growth stage and were well into flowering at the time of analysis. Samples were also digested and analysed for nutrient contents by ICP-OES.

Results:

Field (P only) – wheat and barley

Significant correlations ($p < 0.05$) between XRF and ICP results for wheat and barley samples were not obtained. It appears that the state of the plants severely affected the ability of XRF to measure counts of P in the leaf. This might be due to the reduced density of the leaf with the higher moisture contents. Phosphorus concentrations in many of the samples could not be determined by XRF as they fell below detection limits. Overall P concentrations in the plant tissue were low due to the very low P availability at these sites.

Field (P only) – beans, canola, and field pea

In contrast to wheat and barley above, significant correlations ($p < 0.05$) were obtained for relationships between XRF and ICP for the determination of P contents in beans ($R^2 = 0.71$), canola ($R^2 = 0.9$) and field pea ($R^2 = 0.95$). Possible explanations for the excellent correlations obtained for these crop types and not wheat and barley are:

- 1) Overall plant P concentrations at Hart were higher potentially due to greater soil P levels allowing improved detection of P by XRF
- 2) The more advanced growth stage of these crops meant that the moisture content in the leaves were lower further aiding detection ability by XRF.
- 3) By measuring older to younger leaves the variation in P concentration was significantly greater than that obtained for wheat and barley.

Laboratory (P only):

Drying the leaf samples allowed for significantly ($p < 0.05$) moderate correlations between XRF and ICP determined P concentrations for both wheat ($R^2 = 0.6$) and barley ($R^2 = 0.49$). This further evidence that removal water content in the leaf improves the ability of XRF to measure P. Variation in

P concentrations between upper and lower portions of the leaf was also reduced. Excellent correlations were also obtained for beans, canola and field pea with the relationship for beans increasing upon drying of the leaf.

Combining all crop data for samples that have been dried and analysed by XRF with ICP determined P concentrations produces an excellent correlation suggesting minimal matrix effects of each crop type on XRF P determination.

Correlation coefficients (R^2) for other nutrients that can be measured by XRF both in the field and in the laboratory with ICP measured concentrations were presented in the 2014 progress report. It appears XRF is a useful tool to measure Ca (all crops) and S (beans, canola and field pea) but might not be appropriate for K. Drying the leaf samples improved XRF detection and subsequent relationships with ICP.

Grain analysis by XRF

Similar to the protocol for green leaf material grain samples were analysed in the field before processing in the laboratory. Three points (top, middle, bottom) of single grain heads from 60 plots (30 barley samples and 30 wheat samples) that had varying rates of P at Sherwood were analysed by XRF. The grain heads were then threshed and analysed again by XRF on whole grains with chaff removed. The grains were then ground and analysed once more by XRF before nutrient content determination occurred through acid digestion followed by analysis by ICP.

XRF was unable to measure nutrient concentrations of intact grain samples apart from Zinc which produced excellent correlation coefficients ($R^2 = 0.77$ – barley, 0.72 – wheat (see supporting document)). Whole grain analysis enabled significant ($p < 0.05$) correlations for both wheat and barley although they were relatively low ($R^2 = 0.25$ – barley, 0.33 – wheat). Again XRF performed well for Zinc on these samples. In comparison to the original dataset for prepared (ground) grain samples the amount of P detected on the XRF was substantially lower (figure 2) which shows that proximity of sample to XRF window is important for P detection.

By grinding the grain samples XRF was able to accurately measure the P concentration in grain samples and results appeared to fit well with the previous dataset on grain samples (figure 2).

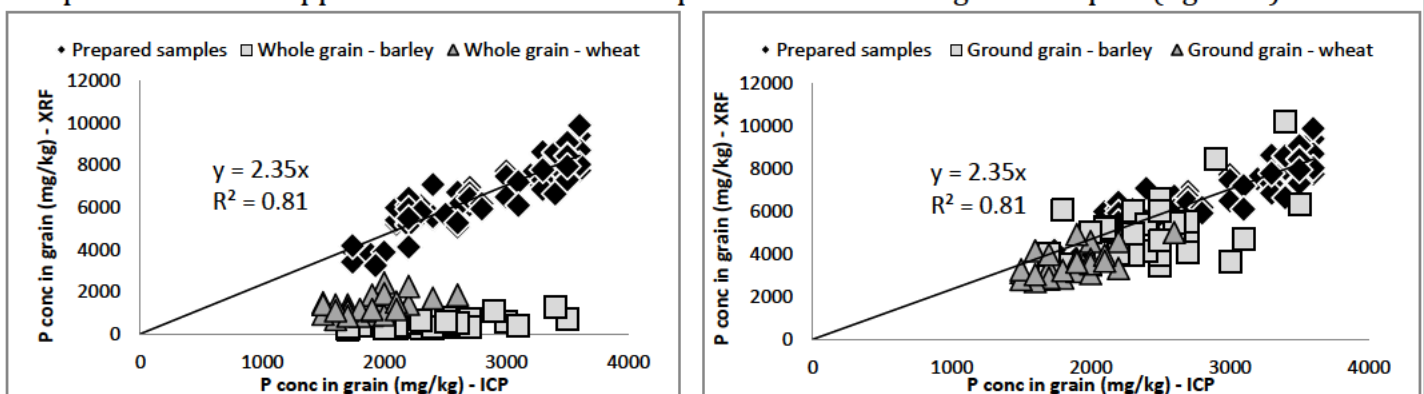


Figure 2: Relationships between P concentrations in grain determined by ICP and that determined by XRF from whole grains (left) and ground grain (right). Both samples sets are compared to the original dataset of prepared grain samples.

Conclusions Reached &/or Discoveries Made (Not to exceed one page)

Please provide concise statement of any conclusions reached &/or discoveries made.

XRF technology enables rapid, cost effective and highly accurate determination of selected nutrient concentrations (Ca, K, P, S and Zn) in a wide range of crop types applicable to S.A. broad acre agriculture that have been sufficiently prepared (dried and ground). The inbuilt calibrations of the XRF

instrument used in this project won't accurately provide the nutrient concentration result and therefore calibration equations are required to be built. One calibration parameters have been produced they can be accommodated into the XRF machine allowing for direct output of correct concentrations. Analysis by XRF in the field on selected crop types showed promise in determining nutrient concentrations in situ however crop moisture contents reduced the sensitivity of XRF analysis particular at very low concentrations of P as an example. Removing plant moisture upon drying significantly improved the sensitivity of XRF and enabled highly accurate determination of selected nutrients in leaf material. XRF was unable to accurately measure nutrient concentrations of intact grain heads in the field apart from Zinc which performed well. For accurate measurement of nutrients in grain, samples needed to be ground as whole grain analysis improved from the field results but wasn't as accurate as ground samples. Overall there appears to minimal matrix effects of each crop type in correlations between XRF and ICP determined nutrient concentrations. Additionally relationship parameters between XRF and ICP were very similar between dry matter plant samples and ground grain samples and therefore potentially one calibration equation could be used for all crop types and growth stages.

Intellectual Property

Please provide concise statement of any intellectual property generated and potential for commercialisation.

This project has generated significant intellectual property as this is the first known study that as assessed the performance of XRF for measuring various crop nutrients in situ. In addition XRF calibration datasets have been developed for crop types not previously studied.

The type of XRF used in this project can be purchased from various sources with portable analytical solutions supplying to Australia. Therefore any farming group and commercial soil/plant testing company can purchased the technology.

Application / Communication of Results

A concise statement describing activities undertaken to communicate the results of the project to the grains industry. This should include:

- *Main findings of the project in a dot point form suitable for use in communications to farmers;*
- *A statement of potential industry impact*
- *Publications and extension articles delivered as part of the project; and,*
- *Suggested path to market for the results including barriers to adoption.*

Note that SAGIT may directly extend information from Final reports to growers. If applicable, attach a list of published material.

Main findings of the project in a dot point form suitable for use in communications to farmers;

- XRF has shown considerable potential to measure selected nutrients in various crop species applicable to S.A. broad acre agriculture with the potential to reduce costs and turnaround time of results.
- Sample preparation improves results but portable XRF has also shown to be of some promise for selected nutrients in the field by analyzing samples in situ.
- By removing plant moisture but without any further sample preparation an accurate assessment of plant nutrient concentrations can be obtained with use of XRF.

A statement of potential industry impact

By utilizing XRF technology, advisors, agronomists, researchers have access to rapid and cost effective analysis of selected nutrient concentrations of a wide range of crop species.

Publications and extension articles delivered as part of the project;

- Abstract submitted and accepted at the Soil Science Australia conference held in Melbourne 23rd-27th November 2014 titled “Does PXRF allow for in situ analysis of elements in crop species?”
- Presentation at the Soil Science Australia conference held in Melbourne 23rd-27th November 2014 titled “Does PXRF allow for in situ analysis of elements in crop species?”
- Article produce by Ag communications appeared in the Stock Journal (28/05/2015)
- YouTube clip featuring XRF technology appears on the SAGIT facebook page.
- XRF displayed at the Karoonda field day (01/09/2015) with complementary article in the field day booklet which will also appear on the MSF website.

Suggested path to market for the results including barriers to adoption.

It would be recommended that anyone that would like to purchase and use XRF technology for plant nutrient analysis build on calibrations developed in this project. XRF would be most likely suited to groups that do routine plant sampling and XRF can be used as a screening tool to prioritise samples for analysis in order to save cost associated with sending numerous plant samples to a laboratory. Similar to NDVI, XRF could be used by researchers to aid field trial analysis without the added cost of laboratory analysis.

Barriers to market could possibly be the perceived risk of radiation which is emitted from the XRF. XRF uses and instrumentation are required to be registered with the EPA.

Unfortunately the technology appears to be restricted to the analysis of Ca, K , P, S and Zn.

POSSIBLE FUTURE WORK

Provide possible future directions for the research arising from the project including potential for further work and partnerships.

As with any new technology that is proposed as an improvement in terms of cost and time to an established laboratory method calibration datasets need to be extensive. Significant amount of sample numbers will improve the robustness of calibration sets and provide greater confidence for the user to accurately interpret the results from the XRF in this case.

Obtaining greater amount of sample numbers in the calibrations sets produced from this report will only aid in the uptake of XRF technology. While we have the instrument available sample numbers will increase in association with our other SAGIT project utilising P responsive trials.

Use of XRF in the agricultural industry is very new but the technology has been used for some time in the mining industry and also by contaminant companies to assess various amounts of elements in rocks and soils. Preliminary assessment of selected soil samples has shown that XRF could accurately predict CaCO₃ contents using the measurement of Ca as a surrogate for CaCO₃. If proven to be accurate XRF has the potential to map CaCO₃ contents throughout paddocks relatively cheaply which has significant impacts on P nutrition. XRF as a total measurement of elements in soils may have some other benefits to other soil test measures.

While not central to S.A. broad acre agriculture, XRF has the ability to accurately measure silica contents in various crop types. In collaboration with University of New England an initial calibration set has been established. The normal acid extract used for the determination of element concentrations in plants is not strong enough to dissolve all the silica and therefore it is disregarded. As a result Si analysis in crop plants is significantly underestimated. For accurate determination of Si in plants the

samples need to be digested in hydrofluoric acid which is time consuming and due to the safety impacts of using HF acid the method is not routinely used in commercial laboratories.

AUTHORISATION
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Position: Research Fellow

Signature:
Date: 03/09/2015

Submit report via email to admin@sagit.com.au as a Microsoft Word document in the format shown ***within 2 months*** after the completion of the Project Term.