Potential and application of X-ray fluorescence spectrometry to estimate iron and zinc concentration in potato tubers

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The development of new biofortified potato clones from the International Potato Center’s breeding program, grown in 3 distinct locations of Peru. Twenty clones showing high iron concentration (above 32 mg/kg DW) and 13 clones with high concentration of zinc (above 25 mg/kg DW) were identified. X-ray fluorescence spectrometry provides a rapid, low-cost and suitable tool for potato breeders, compared to inductively coupled plasma optical emission spectrometry for screening iron and zinc concentrations, especially when a high number of potato clones must be evaluated in a short time frame.

1. Introduction

Biofortification is the approach through which micronutrient-dense staple crops are developed to help reduce hidden hunger, the micronutrient deficiency in the diet due to the lack of essential vitamins and minerals. Hidden hunger is a major public health problem in developing countries, associated with illness, blindness, premature death, reduced productivity, and impaired mental development, which afflicts more than 2 billion people worldwide (von Grebmer et al., 2014). Biofortification is complementary to supplementation and fortification that can contribute to diminish iron (Fe), zinc (Zn) and vitamin deficiencies, having a positive influence on human health. It has the advantage of providing a feasible means of reaching malnourished rural human populations, who have limited access to commercially marketed fortified foods and supplements (Bouis et al., 2013) and do not consume sufficient amounts of animal food sources containing these micronutrients in significant concentrations.

Several years ago, under the umbrella of the HarvestPlus Program (http://www.harvestplus.org/), which leads a global interdisciplinary alliance of research institutions and implementing agencies for developing biofortified varieties of staple crops, the International Potato Center (CIP) initiated the development of Fe and Zn biofortified potatoes. Wide genetic diversity for Fe and Zn concentrations has been reported in potato tubers (Bonierbale et al., 2010). A screening of potato germplasm at CIP found concentrations of 11–30 mg/kg dry weight (DW) of Fe and 8–25 mg/kg DW of Zn in landraces and improved cultivars, and studies on genotype by environment interactions for Fe and Zn found significant effects, but these did not result in drastic changes of the relative ranking of genotypes (Burgos et al., 2007). Heritability of Fe and Zn concentrations in potato tubers is relatively high, and no negative correlations were found between micronutrient concentrations and important resistance or utilization traits (Paget et al., 2014). Furthermore, a recent study found that 63 to 79% of the potato Fe is released from the food matrix after gastrointestinal in vitro digestion, and therefore is available for absorption at the intestinal level. This means that, the bioaccessibility of Fe in potato tubers is significantly higher, compared to other crops such as wheat and beans (Andre et al., 2015).

The development of new biofortified potato populations involves the evaluation of thousands of genotypes. Breeders have estimated that it is possible to reach a concentration of 48 mg/kg DW for Fe and 33 mg/kg DW for Zn (Bonierbale et al., 2007) by conventional breeding.

Inductively coupled plasma optical emission spectrometry (ICP-
OES) is the most accurate method used for analyzing minerals in plant tissues and food products (Boss and Fredeen, 1997) and determines the concentrations of 14 minerals with high sensitivity (Wheal et al., 2011). The fact that some of the minerals detectable by ICP-OES such as aluminum (Al), chromium (Cr) and titanium (Ti) are not present in plant tissues permits assessments of potato tuber samples for contamination with minerals from other sources like soil, dust or inappropriate processing equipment (Porras et al., 2014). However, ICP-OES analysis is time consuming and requires expensive equipment, highly qualified staff for routine analysis, sample digestion, toxic reagents and daily instrument calibration using standard solutions.

Non-destructive X-ray fluorescence spectrometry (XRF) is used broadly for fast mineral analysis in the cement industry, mining, archaeology, geology and in medical applications (West et al., 2007; Yao et al., 2015). XRF is an analytical method based on the excitation of electrons by incident X-radiation. When a sample is irradiated with X-ray energy emitted from an X-ray tube, fluorescent X-rays are generated in the sample and can be measured for quantification of its constituent elements in the detection system, which recognize the received photons. Ejection of electrons from inner atomic shells creates vacancies which are filled by electrons falling back from the outer shells. Amounts of fluorescence energy emitted are characteristic for particular elements (Paltridge et al., 2012a; Stankey et al., 2015; Yao et al., 2015). The concentration of minerals in analytical samples is estimated by comparison with a calibration, which is obtained by relating the intensity of X-ray emissions for each individual mineral in a set of samples to its reference concentration previously determined by ICP-OES, with which the quantitative analysis is performed (Paltridge et al., 2012a; Yao et al., 2015).

A great advantage of the XRF technique compared to ICP-OES is that the measurement can be carried out directly on solid samples. This avoids the use of toxic and corrosive acids, which will drastically reduce environmental pollution, and significantly saves time and costs (Perring and Andrey, 2003; Noda et al., 2006; Reidinger et al., 2012; Mir-Marqués et al., 2016). XRF is not as highly dependent on operator skills during routine analysis, as other equipment for chemical analyses are, and it provides highly reproducible results (Otaka et al., 2013; Stankey et al., 2015).

XRF has been applied for evaluation of minerals in food crops and products. For example, it was applied in the determination of phosphorus, sulfur, chlorine, potassium, calcium, Fe and Zn in milk powder (Perring and Andrey, 2003); calcium, potassium, phosphorus, Fe, Zn, magnesium and sodium in ultra-filtered milk and yoghurt (Rinaldini et al., 2009); phosphorus, potassium, calcium, magnesium, nickel and Zn in coffee leaves and branches (Tezotto et al., 2013); magnesium, phosphorus, chlorine, potassium, manganese, copper, bromine and barium in soybean (Otaka et al., 2013) and sodium in cheese (Stankey et al., 2015). XRF has also been applied to estimate the phosphorus content in potato starch, helping to predict pasting characteristics (Noda et al., 2006).

During the past years, XRF technology has been adapted for several HarvestPlus crops and has been demonstrated to be a promising technology for estimating Fe and Zn concentration in beans, rice, pearl millet, maize, cowpea and wheat (Guild et al., 2017). However, the potential of using XRF for analyzing mineral concentrations in potato tubers and other root and tuber crops has not yet been reported. The aim of this study was to evaluate the potential of applying XRF to estimate Fe and Zn concentration in a high number of freeze dried and milled potato tuber samples in CIP’s breeding program for the selection of biofortified potato clones with high Fe and Zn values.

2. Materials and methods

2.1. Plant material

A set of 80 samples from the Fe and Zn biofortified potato population at CIP within the HarvestPlus Program was used for calibration development and external validation. The 80 samples, which have a large variation in Fe and Zn concentration as determined by ICP-OES analysis, were obtained from a trial planted in Huancayo (3200 m.a.s.l.), Junín, Peru. A second set of 128 samples from CIP’s native potato collection was used for independent validation. The 128 samples were obtained from a trial planted in Pataz (2780 m.a.s.l.), La Libertad, Peru. The resulting XRF calibration was then used to estimate the Fe and Zn concentration in biofortified clones grown in 3 locations of Junín, Peru: 257 clones planted in La Victoria (3265 m.a.s.l.), in September 2012 and harvested in March 2013, 154 clones planted in Comas (3335 m.a.s.l.), in March 2013 and harvested in September 2013, and 207 clones planted in Huancanci (3800 m.a.s.l.), in November 2013 and harvested in June 2014.

2.2. Preparation of freeze dried and milled potato tuber samples

We followed the sampling and sample preparation procedures of Porras et al. (2014). Harvested potato tubers were processed as follows: raw tubers were washed thoroughly with tap water to remove any residue from soil, rinsed with deionized, distilled water, patted dry with paper towel and peeled. Tubers were then cut longitudinally from stem to bud end into four sections. Two or three slices were taken from two opposite sections of each tuber to obtain a 50 g sample, which was frozen, freeze dried, milled with 0.425 mm grid (40 mesh) to ensure particle sizes were similar, and stored in polypropylene bags before mineral analysis.

2.3. Reference analysis

All freeze dried and milled potato tuber samples to be used in calibration and validation were analyzed by ICP-OES using a nitric acid/perchloric digestion method (Wheal et al., 2011) at Waite Analytical Services (WAS) Laboratory of Adelaide University, Australia.

2.4. XRF

The freeze dried and milled material (3–4 g per sample) was scanned by XRF using an X-Supreme 8000 (Oxford Instruments, Abingdon, UK), an energy-dispersive XRF spectrometer equipped with a tungsten X-ray tube and fitted with a 10-place auto-sampler holding 40 mm Al cups. The scans were conducted in Al cups lined with 30 mm polypropylene inner cups sealed at one end with 4 μm thick Poly-4 resistant film (Oxford Instruments, Abingdon, UK), as is common standard for the analysis of powdered samples. Measurement conditions were almost identical to those reported previously for the XRF analysis of Fe and Zn in wheat, rice and pearl millet (Paltridge et al., 2012a, 2012b), but using detection time of 100 s for each element (Table 1). The total analysis time for each sample was 270 s, which included 100 s acquisition times for the different Zn and Fe conditions as well as 70 s dead time for establishing each measurement condition.

| Table 1 | XRF conditions used for the analysis of potato samples. |
|---------|--------------------------------------------------------|
| Conditions | Iron | Zinc |
| Atmosphere | Air | Air |
| Detector | SDD | SDD |
| Tube filter | A6 | W5 |
| Secondary beam filter | open | open |
| Voltage (V) | 15 | 26 |
| Set current (μA) | 200 | 115 |
| Acquisition time (s) | 100 | 100 |
2.5. Calibration and validation

To calibrate the XRF instrument, ICP-OES reference concentration for Fe and Zn from 40 potato samples were registered into the X-Supreme software before each sample was scanned. The relationship between intensity of radiation and ICP-OES reference values was then established, using the XRF calibrate function and linear regression model (Stankey et al., 2015). The validation of the calibration was done using an additional 40 potato samples analyzed by ICP-OES. Correlations between XRF values and reference values were examined along with bias and standard error of prediction (SEP) (Paltridge et al., 2012b; Reidinger et al., 2012).

2.6. Statistical definitions

The statistical calculations were based on Perrign and Andrey (2003) for determination of bias, standard error of the calibration (SEC) based on the differences between each reference value and those calculated using the calibration model, SEP and limit of quantification (LOQ).

3. Results and discussion

3.1. Reference values

The Fe and Zn concentration of the 80 freeze dried and milled potato tuber samples ranged from 10 to 33 mg/kg DW and from 9 to 29 mg/kg DW, respectively. This range of variation covers previously reported ranges of variation of Fe and Zn in potato tuber samples (16–33 mg/kg for Fe and 8–20 mg/kg for Zn by Burgos et al. (2007)) and hence was considered sufficient to obtain robust XRF calibrations.

Mineral analysis in root and tuber crops is more difficult compared to grain crops, because the risk of soil particle contamination is greater. Al and Ti are common elements in soils but are only present in trace levels in plant materials; hence these minerals are used as indicators of possible Fe and Zn contamination from soil, dust or other particles (Stangoulis and Sison, 2008). Likewise, Cr was used as an indicator of deterioration of materials and equipment utilized for sample preparation.

All the samples used in calibration and validation procedures presented Al concentrations lower than 1 mg/kg DW and Ti and Cr levels below the limit of detection (0.03 and 0.20 mg/kg DW, respectively), indicating their freedom from soil, dust or other contaminants.

3.2. Calibration

Forty samples were used for calibration development and another 40 samples not included in the calibration data set were used for validation of the developed calibration. The calibrations showed high coefficients of determination ($R^2$), 0.93 for Fe and 0.97 for Zn (Fig. 1a and b). Similar $R^2$ have been obtained for XRF calibrations developed to estimate Fe and Zn in coffee leaves and branches (≥0.95) (Tezotto et al., 2013); rice (≥0.85) and pearl millet (≥0.97) (Paltridge et al., 2012b); and Zn in rice (≥0.99) (Teixeira et al., 2012). The SEC was low for both minerals: 1.44 mg/kg DW for Fe and 0.91 mg/kg DW for Zn. Paltridge et al. (2012b) reported lower SEC for a calibration developed to estimate Fe (0.6 mg/kg) and similar SEC for Zn (1.3 mg/kg) in rice. The same authors found higher SEC to estimate Fe (6.3 mg/kg) and Zn (3.6 mg/kg) in pearl millet. The higher and the lower SEC of the potato calibration for Fe compared to rice and pearl millet can be explained by the fact that the range of variation found for Fe in potato is higher than in rice and lower than in pearl millet.

The calibrations developed for potato tubers are empirical calibrations relating the XRF counts (intensity of X-ray emissions) with Fe and Zn concentration as determined by ICP-OES. This approach is directly used from empirical methods for the calculation of element concentrations, where the range of analyte concentrations is restricted, and where sets of standard samples are similar in composition to samples of interest (Paltridge et al., 2012b; Reidinger et al., 2012). Da-Col et al. (2015) demonstrated very good correlations (≥0.97) through a univariate methodology based on peak area calibration in table salt, while Guild et al. (2017) showed the advantages of using a non-matrix-matched calibration in grain crops for calibrating XRF instruments.

3.3. External validation

External validation refers to the validation performed using samples grown under similar environmental conditions (location, year, soil types) but not included in the calibration data set. It is used to test the robustness and accuracy of the model and it demonstrates the reliability of the calibration equation for mineral analysis of further samples grown under similar environmental conditions.

In our study, 40 samples not included in the calibration data set were used for external validation by comparing estimated XRF values and ICP-OES reference values in the 40 samples. The ranges (11 to 32 mg/kg DW and 12 to 25 mg/kg DW for Fe and Zn, respectively) were similar to the range of Fe and Zn in the samples used for calibration development. The $R^2$ for the validation was high, 0.96 for Fe and 0.93 for Zn (Fig. 1c and d), indicating that these elements can be estimated by XRF in potato tubers with very high precision. SEPs were 1.10 mg/kg DW for Fe and 0.99 mg/kg DW for Zn, showing that the models have excellent predictive abilities. The bias values were <1 mg/kg DW, estimated in each validation set by subtracting XRF values from corresponding ICP-OES values. The overall SEP observed in our study is similar to those reported in the XRF analysis of rice (Paltridge et al., 2012b), and lower than in grain crops reported by Guild et al. (2017). Mir-Marqués et al. (2016) developed a model for the prediction of Fe and Zn in artichokes that showed that the accuracy of the validation is acceptable for both minerals.

The estimated LOQ in potato tubers for Fe and Zn as determined by XRF was 2 mg/kg DW and 6 mg/kg DW, respectively. LOQ for both minerals were low enough and therefore suitable for routine analysis. Other studies reported LOQ in rice of 3 and 12 mg/kg for Fe and Zn, respectively and in pearl millet 5 and 16 mg/kg for Fe and Zn, respectively (Paltridge et al., 2012b).

As standard reference materials for potato tubers are not available, the precision and accuracy of XRF was checked by analyzing 3 samples with a known concentration of Fe and Zn 8 times. The precision of the developed method was determined by relative standard deviation (RSD) and the accuracy by calculating the recovery (Table 2). A RSD with variability of 1–3% and recoveries between 98 and 105% were found. These values are similar to those reported by Tezotto et al. (2013) who found a good relationship between certified reference materials and data obtained by XRF, with recoveries from 82 to 117%. Teixeira et al. (2012) found an RSD of 3.5% for Zn in rice samples, while Mir-Marqués et al. (2016) reported this parameter lower than 9% for both minerals in artichoke samples.

3.4. Independent validation

The external validation demonstrated the reliability of the developed calibration for Fe and Zn in the analysis of potato tuber samples from the same environment. This does not ensure an accurate Fe and Zn prediction in potato tuber samples grown under other environmental conditions (location, year, soil types). Thus, independent validation using samples from a completely different set of samples than the one used for calibration development is needed.

In our study, independent validation was performed with 128 samples from a different location (Pataz, La Libertad, Peru). The Fe and Zn concentration as determined by XRF were 9 to 29 mg/kg DW and 5 to 15 mg/kg DW, respectively. The $R^2$ values for independent validation were 0.93 and 0.92 for Fe and Zn, respectively (Fig. 1e and f) and
therefore were as high as shown for the external validation. This means that developed XRF calibrations can be applied with high precision in potato tubers grown under different environmental conditions.

3.5. Application of XRF for estimation of Fe and Zn concentration in biofortified clones bred at CIP

The developed XRF calibrations were used for estimating the Fe and Zn concentration of potato tuber samples from CIP’s biofortification breeding program. These biofortified samples were evaluated in three distinct locations in Peru: La Victoria, Comas and Huancani (Tables 3a and b).

On a DW basis, the Fe concentration showed considerable variation at all three sites. The range of variation for the Fe concentration in the clones grown in La Victoria (8 to 29 mg/kg DW) was lower than the range of variation for the Fe concentration in the clones grown in Comas (10 to 36 mg/kg DW) and in Huancani (11 to 39 mg/kg DW). The Zn concentration did not present much variation across the three locations, ranging from 9 to 30 mg/kg DW in La Victoria; from 9 to 31 mg/kg DW in Comas and from 9 to 32 mg/kg DW in Huancani. Eight clones grown in Comas and 12 clones grown in Huancani presented Fe concentration higher or equal to 32 mg/kg DW and 5 clones grown in La Victoria, 6 clones grown in Comas and 2 clones grown in Huancani presented Zn concentration above 25 mg/kg DW. Eight clones grown in Comas and 12 clones grown in Huancani presented Fe concentration higher or equal to 32 mg/kg DW and 5 clones grown in La Victoria, 6 clones grown in Comas and 2 clones grown in Huancani presented Zn concentration above 25 mg/kg DW. Samples of all these clones were sent for ICP-OES analysis at WAS (Adelaide, Australia) and the high concentrations were confirmed by below-threshold levels of the three indicators of contamination (Al, Ti and Cr). Tables 3a and b show Fe and Zn concentration as determined by ICP-OES vs. XRF in all samples sent to WAS. The use of XRF to estimate the Fe and Zn concentration in potato tuber samples is less time consuming and considerably less expensive than the ICP-OES analysis (5 USD against 30 USD per sample). However, it is important to mention that ICP-OES analysis can monitor indicators of contamination, which is not possible with XRF. Hence for extra certainty, samples of high Fe and Zn

Fig. 1. Calibration (a, b), validation (c, d) and independent validation (e, f) curves.
**Table 2**

| Repetition | Sample 1  | Sample 2  | Sample 3  |
|------------|-----------|-----------|-----------|
|            | Fe (mg/kg) | Zn (mg/kg) | Fe (mg/kg) | Zn (mg/kg) | Fe (mg/kg) | Zn (mg/kg) |
| 1          | 27.57      | 22.15     | 21.25     | 17.64      | 13.48      | 14.72      |
| 2          | 27.11      | 23.68     | 20.18     | 17.17      | 13.65      | 14.34      |
| 3          | 27.90      | 23.00     | 20.60     | 18.03      | 13.21      | 14.97      |
| 4          | 27.58      | 21.54     | 20.98     | 17.42      | 13.91      | 14.34      |
| 5          | 27.99      | 22.73     | 21.03     | 17.75      | 13.64      | 14.81      |
| 6          | 27.63      | 23.10     | 21.09     | 17.77      | 13.66      | 15.22      |
| 7          | 27.33      | 22.69     | 20.48     | 18.84      | 14.28      | 15.41      |
| 8          | 28.36      | 21.63     | 20.77     | 18.25      | 14.55      | 15.96      |
| Average (mg/kg) | 27.68      | 22.44     | 20.80     | 17.93      | 13.80      | 14.97      |
| SD         | 0.39       | 0.60      | 0.36      | 0.45       | 0.43       | 0.55       |
| RSD (%)    | 1.42       | 2.67      | 1.72      | 2.49       | 3.15       | 3.67       |
| Recovery (%) | 102.53     | 102.00    | 103.99    | 105.45     | 98.55      | 99.81      |
| ICP (mg/kg) | 27.49      | 21.79     | 20.24     | 17.05      | 13.59      | 14.85      |
| Bias       | 0.68       | 0.44      | 0.80      | 0.93       | 0.20       | 0.30       |

**Table 3a**

Comparison of Fe concentrations in CIP’s biofortified potato clones estimated by XRF and ICP-OES.

| Clones (CIP-Number) | Dry weight (mg/kg) | Dry matter (%) | Fresh weight (mg/kg) |
|---------------------|-------------------|----------------|---------------------|
|                     | XRF ICP-OES       | XRF ICP-OES    |

| (Grown in Comas/Peru) | CIP-311209.002 | CIP-311422.014 | CIP-311200.114 |
|-----------------------|----------------|----------------|-----------------|
|                       | 28.43          | 26.75          | 26.56           |
|                       | 30.90          | 28.98          | 29.04           |
|                       | 23.61          | 20.98          | 16.57           |
|                       | 6.71           | 4.23           | 6.77            |
|                       | 7.30           | 4.81           | 7.63            |

| (Grown in Huancani/Peru) | CIP-311083.021 | CIP-311420.074 |
|-------------------------|----------------|----------------|
|                         | 26.61          | 31.05          |
|                         | 25.63          | 28.11          |
|                         | 20.16          | 24.16          |
|                         | 5.36           | 7.50           |
|                         | 5.17           | 6.79           |

**Table 3b**

Comparison of Zn concentrations in CIP’s biofortified potato clones estimated by XRF and ICP-OES.

| Clones (CIP-Number) | Dry weight (mg/kg) | Dry matter (%) | Fresh weight (mg/kg) |
|---------------------|-------------------|----------------|---------------------|
|                     | XRF ICP-OES       | XRF ICP-OES    |

| (Grown in La Victoria/Peru) | CIP-311083.021 | CIP-311420.074 |
|-----------------------------|----------------|----------------|
|                             | 28.43          | 30.90          |
|                             | 23.61          | 20.98          |
|                             | 6.71           | 4.23           |
|                             | 7.30           | 4.81           |

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References

Andre, C., Evers, D., Ziebel, J., Guignard, C., Hausman, J.F., Bonierbale, M., zum Felde, T., Burgos, G., 2015. In vitro bioaccessibility and bioavailability of iron from potatoes with varying vitamin C, carotenoid, and phenolic concentrations. J. Agric. Food Chem. 63 (41), 9012–9021.
Bonierbale, M., Amoros, W., Burgos, G., Salas, E., Juarez, H., 2007. Prospects for enhancing the nutritional value of potato by plant breeding. African Potato Association Conference Proceedings Conference 7, 26–46.

Bonierbale, M., Burgos, G., zum Felde, T., Sosa, P., 2010. Nutritional composition of potatoes. Cahiers de nutrition et diététique 45, 528–536.

Boss, C.H., Fredeen, K., 1997. Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry. Perkin Elmer, USA.

Bouis, H., Low, J., McKwan, M., Tanumihardjo, S., 2013. Biofortification: Evidence and Lessons Learned Linking Agriculture and Nutrition. FAO and WMO.

Burgos, G., Amoros, W., Morote, M., Stangoulis, J., Bonierbale, M., 2007. Iron and zinc concentration of native Andean potato varieties from a human nutrition perspective. J. Sci. Food Agric. 87 (4), 668–675.

Da-Coli, J., Bueno, M., Melquiades, F., 2015. Fast and direct Na and K determination in table marine, and low-sodium salts by X-ray fluorescence and chemometrics. J. Agric. Food Chem. 63, 2406–2412.

Guld, G., Paltridge, N., Anderson, M., Stangoulis, J., 2017. An energy-dispersive X-ray fluorescence method analyzing Fe and Zn in common bean maize and cowpea biofortification programs. Plant Soil 419 (1–2), 457–466. http://dx.doi.org/10.1007/s11104-017-3352-4.

INEI, 2013. Instituto Nacional de Estadística e Informática. Encuesta Nacional de Demografía y Salud Familiar Lima Perú.

Institute of Medicine (US) Panel on Micronutrients, 2001. Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium and Zinc. National Academy Press (US), Washington, DC.

Lombardo, S., Pandino, G., Mauronicale, G., 2013. The influence of growing environment on the antioxidant and mineral content of early crop potato. J. Food Compos. Anal. 32, 28–35.

Mir-Marqués, A., Martínez-García, M., Garrigues, S., Cervera, M., de la Guardia, M., 2016. Green direct determination of mineral elements in artichokes by infrared spectroscopy and X-ray fluorescence. Food Chem. 196, 1023–1030.

Noda, T., Tsuda, S., Mori, M., Takigawa, S., Matsuura-Endo, C., Kim, S., Hashimoto, N., Yamashita, H., 2006. Determination of the phosphorus content in potato starch using a energy-dispersive X-ray fluorescence method. Food Chem. 95, 632–637.

Otaka, A., Hokura, A., Nakai, I., 2013. Determination of trace elements in soybean by X-ray fluorescence analysis and its application to identification of their production areas. Food Chem. 147, 318–326.

Paget, M., Amoros, W., Salas, E., Eyzaguirre, R., Alsphac, P., Apilaza, I., Noble, A., Bonierbale, M., 2014. Genetic evaluation of micronutrient traits in diploid potato from a base population of Andean Landrace Cultivars® Crop Sci. 54 (5), 1949–1959.

Paltridge, N., Milham, P., Guild, G., Stangoulis, J., 2012b. Energy-dispersive X-ray fluorescence analysis of zinc and iron concentration in rice and pearl millet grain. Plant soil 361 (1–2), 251–260. http://dx.doi.org/10.1007/S11104-011-1104-4.

Perring, L., Andrey, D., 2003. ED-XRF as a tool for rapid minerals control in milk-based products. J. Agric. Food Chem. 51, 4207–4212.

Porras, E., Burgos, G., Sosa, P., zum Felde, T., 2014. Procedures for Sampling and Sample Preparation of Sweet Potato Roots and Potato Tubers for Mineral Analysis. International Potato Center (CIP), Global Program Genetics and Crop Improvement, Lima, Peru (ISSBN 978-92-9060-445-7. 13p.).

Residinger, S., Ramser, M., Hartley, S., 2012. Rapid and accurate analyses of silicon and phosphorus in plants using a portable X-ray fluorescence spectrometer. New Phytol. 195, 699–706.

Rinaldini, A., Campderrós, M., Perez Padilla, A., Perino, E., Fernández, J., 2009. Analytic determinations of minerals content by XRF: ICP and EEA in ultra-filtered milk and yoghurt. Latin Am. Appl. Res. 39, 113–118.

Stangoulis, J., Sisson, C., 2008. Crop Sampling Protocols for Micronutrients Analysis. HarvestPlus Technical Monograph Series. (ISBN 978-0-9818176-0-6).

Stansley, J., Akbulut, C., Romero, J., Govindasamy-Lucey, S., 2015. Evaluation of X-ray fluorescence spectroscopy as a method for the rapid and direct determination of sodium in cheese. Am. Dairy Sci. Assoc. 98, 5040–5051.

Teixeira, A., Quintella, C., Korn, M., Fernandes, A., Castro, M., 2012. Determination of Mn and Zn in rice by energy dispersive X-ray fluorescence spectrometry. Quimica Nova 35 (6), 1133–1136.

Tezotto, T., Favarin, J., Neto, A., Lupino, P., Antunes, R., Mazzafera, P., 2013. Simple procedure for nutrient analysis of coffee plant with energy dispersive X-ray fluorescence spectrometry (EDXRF). Scientia Agricola 70 (4), 263–267.

von Grebmer, K., Saltzman, A., Bird, E., Wiesman, D., Prasai, N., Yin, S., Yohannes, Y., Menon, P., Thompson, J., Sonntag, A., 2014. 2014 Global Hunger Index: The Challenge of Hidden Hunger. International Food Policy Research Institute, Concern Worldwide and Welthungerhilfe, Bonn, Washington, D.C. Dublin.

West, M., Ellis, A., Kregersmer, P., Potts, P., Streli, C., Vanhoof, C., Wobrauschek, P., 2007. Atomic spectrometry update: x-ray fluorescence spectrometry. J. Anal. At. Spectrom. 22, 1304–1332.

Whelan, M., Fowles, T., Palmer, L., 2011. A cost-effective acid digestion method using closed polypropylene tubes for inductively coupled plasma optical emission spectrometry (ICP-OES) analysis of plant essential elements. Anal. Methods 3, 2854–2863.

Yao, M., Wang, D., Zhao, M., 2015. Element analysis based on energy-dispersive X-ray fluorescence. Adv. Mater. Sci. Eng. 2015, 7. http://dx.doi.org/10.1155/2015/290593. 290593.