Making light work: X-ray fluorescence spectroscopy

From radiography in medicine to revising the periodic table of elements, X-ray fluorescence spectroscopy has an interesting past and an even more interesting future in the agri-food sector.

X-rays have been around since 1895 when Wilhelm Roentgen noticed a fluorescent glow coming from crystals on a table next to the cathode ray tube he was working on. He concluded that this was a new type of ray able to excite the electrons in the crystals nearby and causing the phosphorescent glow. This invisible ray, capable of passing through solid material, quickly caught the attention of scientists and medics as advances led to radiography, and in 1896 the technique was used on the battlefield to locate bullets in wounded soldiers.

Analytical applications came in 1909 when Charles Barkla established a link between X-rays and the atomic weight of a sample, which not only led to elemental analysis but to revising the system used for numbering the elements, known today as the periodic table of elements. By later establishing a relationship between frequency (energy) and atomic number, scientists were able to identify elements using X-rays, which is the basis of X-ray spectroscopy today.

X-ray fluorescence applications in agri-food

Capable of analysing solids, liquids and powders, X-ray fluorescence (XRF) has mostly been used in geology and mining applications for rapid screening of rocks and ores. Non-destructive analysis of samples using XRF ensures that samples are preserved for archaeological and geo-archaeological applications to explain the human past. But it is the qualitative and quantitative abilities that have applications in the agri-food sector, and by coupling the 'what' and 'how much' with non-destructive analysis in a range of sample types, scientists at Teagasc have developed this technique to examine soils, sediment, grass, dairy waste and milk powders.

Nutrients and trace elements in grass samples

Nutrients and trace elements in grass can depend on stages of growth and soil type, and elemental analysis of grass is a useful measure of both plant nutrition and ability to meet the minimum requirement of essential elements for animal health in pasture-based systems. Conventional analyses involve strong acid or alkaline digestion followed by analysis of the filtrate by either colorimetric analysis, atomic absorption or inductively coupled plasma (ICP) analysis. In routine analytical laboratories, backlogs are common due to high sample throughput, which then delays farmers receiving results, reducing the results' value. Recently published work by Teagasc (Daly and Fenelon, 2017; Daly and Fenelon, 2018) is the first to evaluate the application of energy dispersive XRF (EDXRF) for grass analysis and provide a method to determine major nutrients (phosphorus [P], potassium [K], magnesium [Mg] and calcium [Ca]), and trace elements (copper [Cu], manganese [Mn], zinc [Zn] and sulphur [S]).

Comparing 'old' and 'new' methods

To evaluate a new method, we needed to assess the level of agreement with conventional techniques or 'gold standard' methods. With access to an existing archive of 600 grass samples with known values of some major nutrients and trace elements in grass P, K, Mg, Ca, Cu, Mn, Zn and S, we compared XRF measurements with ICP values with very positive results. Firstly, XRF measurements of grass samples were carried out using the theoretical equations developed in XRF theory to quantify elements in a sample. While this approach is widely used in geology and pharmaceuticals for pure materials, environmental samples with complex matrices present a bigger challenge. For some elements the theoretical approach worked, but for others, there was a noticeable difference (or bias) in the results. This observation allowed us to

The range of agri-food samples currently being analysed using XRF: biosolids and dairy waste; grass; soil; and, milk powder.

develop empirical calibrations specific to each element by using grass samples as standards, and also to 'matrix match' and fine-tune the theoretical calibrations. In **Figure 1**, to determine the percentage of P in grass, three calibration approaches were compared: an empirical (EMP) (based on grass standards); theoretical (FP); and, a matching library (FPML). Best agreement was observed when empirical and matching library calibrations were used to calibrate the XRF frequencies with concentrations. This work demonstrated that bespoke empirical calibrations improved the accuracy and precision of the results. Using standard samples based on the same matrix type can minimise matrix effects of absorbance and enhancement due to the presence of other elements in the sample. This is especially relevant for environmental samples with complex matrices such as soils, sediments, grains and grass samples. We have found that XRF is a viable alternative to digestive techniques for elemental determination across a range of agri-food samples.

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References

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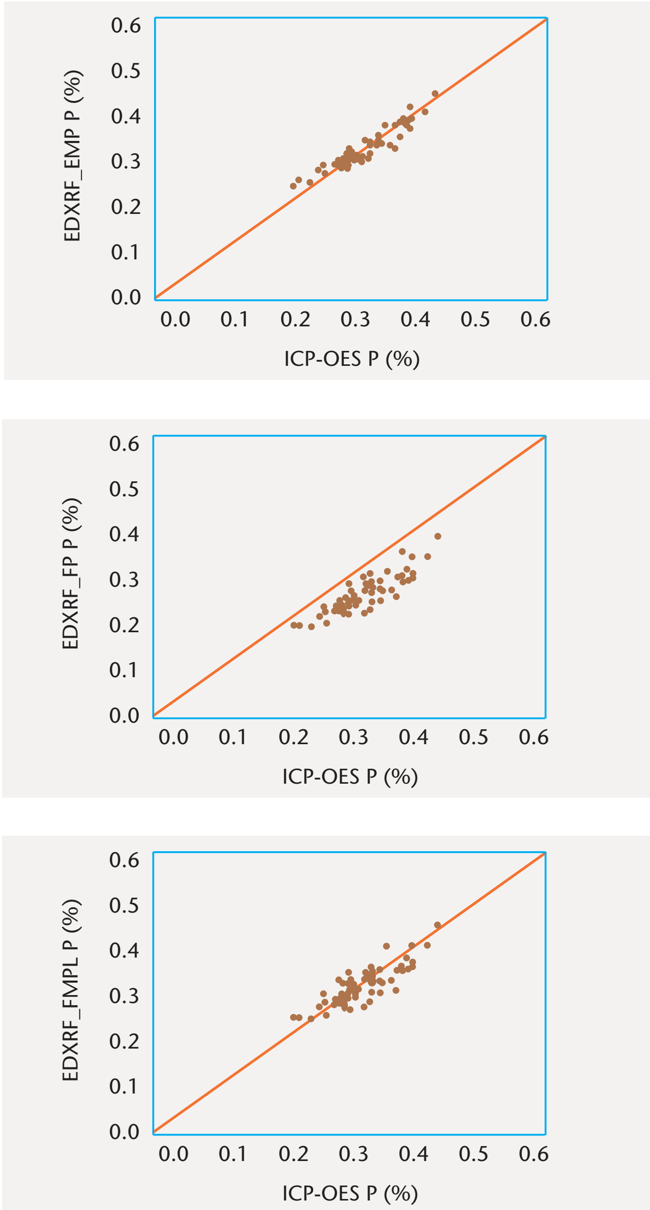

FIGURE 1: Comparison of the percentage P in grass using theoretical calibration XRF, and the improved agreement when empirical grass standards were used.

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