TXRF

TXRF spectrometry applied to food (I): Trace element analysis of plant material

Application Note # XRF 445

Introduction

The analysis of trace elements in plant material is necessary for several reasons. Plants can accumulate toxic elements like heavy metals and, thus are intermediate reservoirs through which these toxic elements from soil, water and air can be transferred to living organisms via the food chain.

In addition essential macro (Mg, P, K, Ca) and trace elements (e.g. Fe and Zn) must be controlled with respect to human nutrition and the fertilization control of agricultural plants. Finally, the presence of abnormally high Br and Cl levels can indicate the illegal application of pesticides or adulterates during the process of food production.

The most common analytical techniques for macro and trace element analysis are inductively-coupled plasma optical emission spectroscopy (ICP-OES) and inductively-coupled plasma mass spectroscopy (ICP-MS). However, the organic matrix of plant materials may cause analytical bias and block the sample introduction systems if not fully dissolved. For the decomposition procedures like high-temperature oxidation (dry ashing) or wet digestion using strong acids or oxidising solvents are applied. These procedures are laborious and take at least two hours for preparation applying most modern high-throughput digestion methods [1].

Even though TXRF spectroscopy shows some specific element limitations, it can be an alternative or complementary analytical technology for raw materials and finished products in food processing.

In order to test the possibilities and restrictions of TXRF spectroscopy, four certified reference materials (NIST 1515 apple leaves, NIST 1547 peach leaves, NIST 1572 citrus leaves and NIST 1573 tomato leaves) were analyzed.

Instrumentation

All measurements were performed using the benchtop TXRF spectrometer S2 PICOFOX. This instrument is equipped with an air-cooled low power X-ray tube (Mo target), a multilayer monochromator with 80% reflectivity and the liquid nitrogen-free XFlash® silicon drift detector (SDD) with an energy resolution of <150 eV (Mn Kα).

Sample preparation and analysis

All standard samples were available as ground powder passed through a sieve of 40 mesh. As this grain size is not suitable for TXRF measurements, the samples were ground in a mixer mill (Retsch MM400, Zr grinding jar) for 3 min at 30 Hz.

An amount of 60–70 mg of the ground powder was weighed, transferred to a polypropylene cryo-tube and suspended in 2.5 ml of a 1 vol % aqueous Triton X-100 solution. Internal standardisation was performed by adding 10 µl of a gallium solution (1 g/l).

For separating the grains, all samples were placed in an ultrasonic bath for 15 minutes. Subsequently they were carefully homogenised and 10 µl of sample suspension were transferred to siliconised quartz glass sample carriers and dried in vacuum. In order to test the analytical reproducibility a tenfold preparation and analysis with a measurement time of 1000 s was performed.
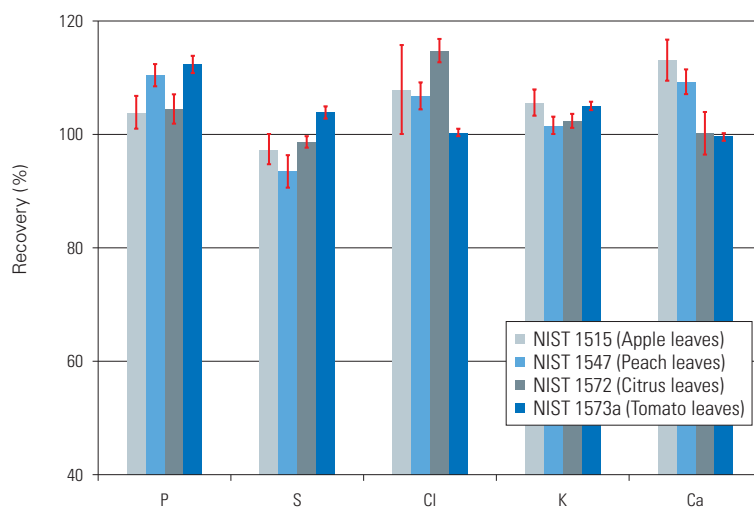

Figure 2

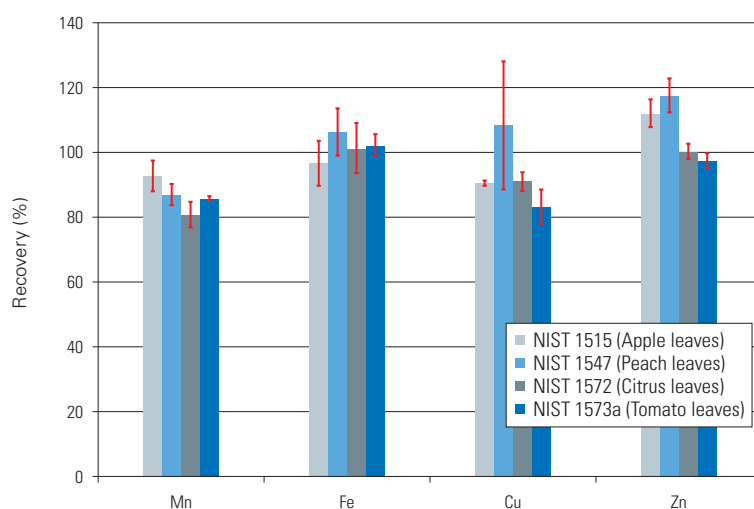Recovery of macronutrients in different plant standards (red bars indicate standard deviation)

Figure 3

Recovery of micronutrients in different plant standards (red bars indicate standard deviation)

Results

The measurement results for the main elements P, S, Cl, K and Ca (Figure 2) show a good concordance of measurement and reference results covering a broad concentration range from about 300 mg/kg to almost 5 %. The same is true for the transition metals Mn, Fe, Cu and Zn (Figure 3), which are present in the low (3.7 mg/kg) to high (320 mg/kg) ppm-range. Several other trace elements could be determined in the plant material samples (Figure 4) ranging from sub-mg/kg up to the high mg/kg-range. Several of these element concentrations are not certified, but they are in good concordance with TXRF results.

The 3 sigma detection limits are displayed in Figure 5. For Ca and lighter elements the detection limits are above 1 mg/kg. Heavier elements can be detected at levels below 1 mg/kg.

Figure 4

Comparison of TXRF and reference values for other trace elements in plant standards; NIST 1515: V, Br, Rb, Sr, Ba, La, Ce, Nd, Pb; NIST 1547: V, Br, Rb, Sr, Ba, Ce, Pb; NIST 1572: Cr, Br, Rb, Sr, Pb; NIST 1573a: V, Cr, As, Br, Rb, Sr, Ba

Conclusions

The analysis of trace elements in plant material can be easily performed with TXRF spectrometry. TXRF does not require any time-consuming sample digestion with hazardous chemicals. Just a simple grinding step followed by preparation of a suspension allows a fast and accurate multi-element analysis.

Macronutrients available in higher concentrations can be measured from low ppm concentrations up to the percent range with an accuracy of about 5 %. For micronutrients and other traces detection limits down to 100 µg/kg can be achieved.

An unique highlight of TXRF analysis is the ability to measure smallest sample amounts. Rare plant material or medical herbs can be directly and quantitatively prepared in a micro reaction vial as described on the last page.
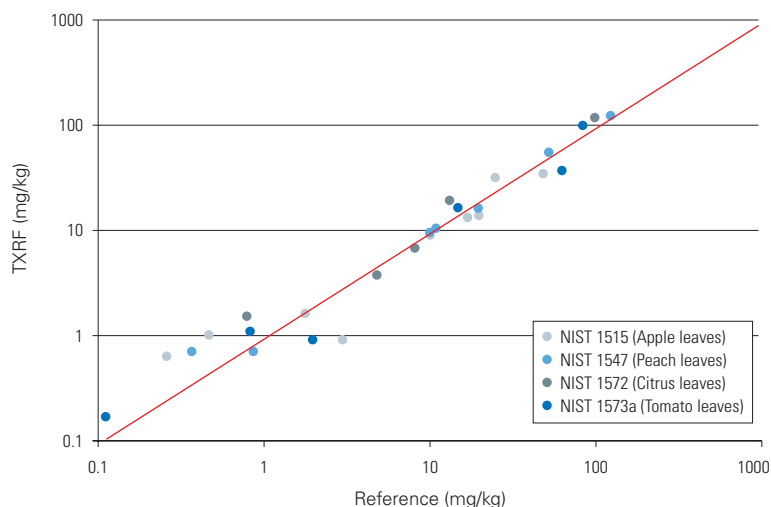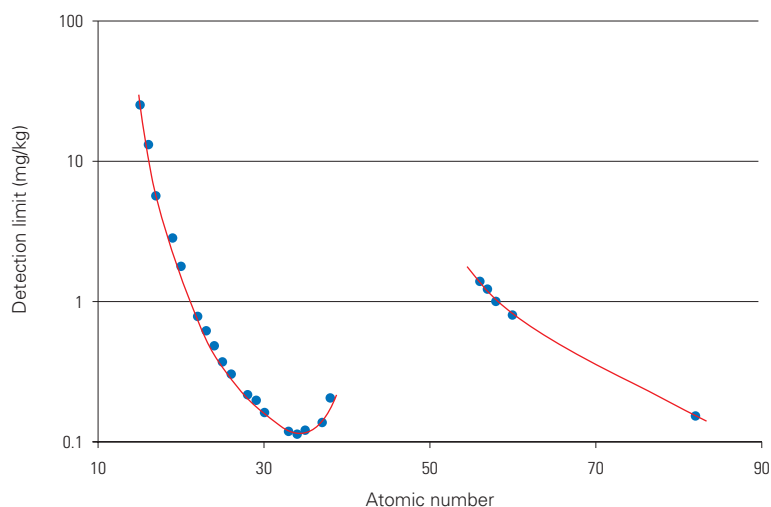

Figure 5

Detection limits for trace elements in plant standards determined by TXRF analysis

Preparation of micro samples in a mixer mill

Smallest amounts of sample, such as are normally used for the analysis of medical herbs or animal tissues, can be prepared in disposable reaction vials. Adapter racks of PTFE which accommodate either 5 or 10 disposable reaction vials can be used for this. In the mixer mills (e.g. Retsch MM 400), samples are ground so quickly and efficiently that no additional cooling is necessary.

The quantitative sample preparation for micro samples is as follows:

- Weigh a few mg of sample and take a note of the exact weight

- Add Triton X-100 and internal standard

- Homogenize in mixer mill

- Pipette 10 µl suspension on a quartz sample carrier

References

[1] Hansen, T.H. et al. (2009) "Micro-scaled high-throughput digestion of plant tissue samples for multi-element analysis", Plant Methods, 5:12

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