TXRF ANALYSIS OF VEGETAL FOODSTUFF SAMPLES

R. Dalipi [1], *E. Marguí* [2], *L. Borgese* [1], *F. Bilo* [1], *G. Zappa* [3], *C. Zoani* [3], *E. Sangiorgi* [4] *and L. E. Depero* [1]

[1] Department of Mechanical and Industrial Engineering, University of Brescia, Via Branze 38, 25123 Brescia, Italy
[2] Department of Chemistry, University of Girona, Campus Montilivi, 17071 Girona, Spain
[3] ENEA, Italian Agency for New Technologies, Energy and Sustainable Economic Development, Casaccia Research Centre, Via Anguillarese 301, 00123 Roma, Italy
[4] Istituto Zooprofilattico Sperimentale della Lombardia e dell'Emilia Romagna "Bruno Ubertini", Via Antonio Bianchi 7/9, 25124 Brescia, Italy

E-mail: rogerta.dalipi@unibs.it

Abstract – In this work, a fast and simple analytical method has been developed for the multi elemental analysis of different vegetal foodstuff samples, by using a combination of two low power benchtop total reflection X-ray fluorescence (TXRF) systems. The suspension of the powdered samples in de-ionized water showed to be the most suitable way for the preparation and analysis of this kind of samples. However, for comparison purposes the samples were also acid digested and measured by TXRF.

Keywords: TXRF, Suspension, Vegetable foodstuff, Mo X-ray tube, W X-ray tube

1. INTRODUCTION

Vegetables are a fundamental part of human diet and are the primary recipients of elements from the environment. Most elements present in vegetables are biochemically important for human health. For example, Co, Cr, Cu, Fe, Mn, Mo, Se and Zn are required for normal plant growing, animal and human nutrition [1]. However, a high concentration intake can be toxic, since these elements are transferred to humans directly, for example through fruits and vegetables, or indirectly through milk and meat from those animals that consume the plants [2]. In view of this situation, the knowledge of elemental composition of vegetable foodstuff is important for safety and nutritional reasons [3].

Usually, spectroscopic techniques such as inductively coupled plasma-mass or atomic emission (ICP-MS or ICP-AES) spectrometry are used for elemental analysis of vegetable foodstuff [4, 5]. The use of these techniques involves a digestion step for destruction of sample matrix. Dry ashing and wet digestion methods are usually employed for this purpose [6]. However, this is time consuming and losses of analytes of interests may occur. Alternatively, microwave ovens have been used to provide faster and better sample digestion, to reduce the amount of reagents used as well as to avoid sample contamination and losses of analytes by volatilization [7].

More and more methods that implicate less or no sample pretreatment for elemental analysis of foodstuff samples and for screening purposes are required.

Most X-ray fluorescence techniques are suitable for this purpose. They present the possibility to perform direct elemental analysis of solid samples, qualitative, semi-quantitative and quantitative determination in a wide dynamic range [8].

TXRF is a variation of energy dispersive X-ray fluorescence spectrometry that has a higher sensitivity and limits of detection at ppb level [9]. TXRF has different advantages over other multi-elemental spectrometric techniques such as low amount of sample, fast and simpler quantification by internal standardization and no matrix effects. Moreover, new low power benchtop TXRF systems are cost-effective since they do not require gas or cooling media for operation.

TXRF has been successfully employed for the analysis of vegetable samples. However, most of contributions deal with sample digestion prior to TXRF analysis and employing large-scaled TXRF instrumentations with high-power X-ray tubes [10].

The aim of this work was to develop a fast and reliable analytical method in combination with low power TXRF systems, equipped with Mo or W X-ray tubes, for multi elemental analysis of different certified reference materials (CRMs) and real vegetal samples.

Firstly, a preliminary study based on the use of Mo TXRF system was performed for comparing two sample treatment procedures: digestion vs suspension. For this purpose, a set of 4 CRMs was analyzed. After that, a more detailed study based on the use of W TXRF system was performed. Method accuracy was evaluated by comparing the TXRF values with certified ones.

2. EXPERIMENTAL

A set of four certified reference materials and three real vegetal samples provided by National Institute of Standards & Technology (NIST) and Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) were analyzed (see table 1).

Table 1. CRMs and real vegetal samples analysed by TXRF.

Vegetal foodstuff samples	**Description**
CRM 1515	Apple leaves
CRM 1547	Peach leaves
CRM 1570A	Spinach leaves
CRM 1573A	Tomato leaves
RM 001	Mushrooms
RM 003	Strawberries
RM 004	Peeled canned tomatoes

The samples were prepared by suspending about 20 mg of powdered sample in 1 mL of de-ionized water or Triton X-100 (1%) solution. Gallium was added as internal standard with a final concentration of 10 mg/L. Samples were also sonicated for a total time of 5 min. Triplicates were prepared for each sample and 10 µL were deposited on a siliconized quartz reflector and dried by IR lamp.

A microwave acid digestion, based on the EPA method 3052, was also employed. About of 250 mg of sample was put in PTFE vessel with 9 mL of nitric acid and 1 mL of hydrogen peroxide. The digestion program consisted in two steps: a first step of 5 min to reach 180 °C and a second step of 10 min at 180 °C. The digested sample solutions were transferred to a 30 mL flask and brought to volume with ultrapure water. An aliquot of 1 mL of each sample digest was fortified with a suitable volume of a Ga solution to have a final concentration of 10 mg/L. The sample deposition volume and drying mode to perform TXRF analysis were the same as for the suspended samples.

In table 2 are shown the TXRF characteristics and measurement conditions of both TXRF spectrometers.

Table 2. Instrumental setup and measurement conditions of TXRF spectrometers.

TXRF system characteristics		
Anode	Mo	W
X-ray tube	Air-cooled metal ceramic	Air-cooled metal ceramic
Power	40 W	50 W
Optics	Multilayer monochromator (17.5 keV)	Multilayer monochromator (35 keV)
Detector	Silicon drift detector, Area: 30 mm^2, FWHM: 139.43 eV (Mn Kα)	Silicon drift detector, Area: 10 mm^2, FWHM: 146.72 eV (Mn Kα)
Atmosphere	Air	Air
Voltage	50 kV	50 kV
Current	750 µA	1000 µA
Measuring time	600 s	2000 s

3. RESULTS AND DISCUSSION

3.1. Accuracy evaluation

The accuracy of the method was evaluated by determining K, Ca, Mn, Fe, Cu, Zn, Rb, Sr and Pb in the four CRMs. Two sample preparation procedures were evaluated: suspension and the conventional acid digestion. Measurements were performed by the Mo TXRF system.

As an example, in Figure 1, typical raw spectra of CRM 1570A measured by both TXRF systems are shown. As we can see, the main differences between Mo and W excitation are regarding the measurement energy (keV) range and the produced background. In both TXRF spectra Si K-lines from quartz glass sample carrier and Ar K-lines from the atmospheric air are detected. The Kα and Kβ peaks of IS (Ga) are also observed. In Mo TXRF spectrum, the strong peak around 17 keV is due to the elastic (Mo Kα) and inelastic (Compton) scattering of the primary X-ray source used for excitation of the sample. On the other way, a bremsstrahlung continuum radiation is produced when a W target is used to generate X-rays.

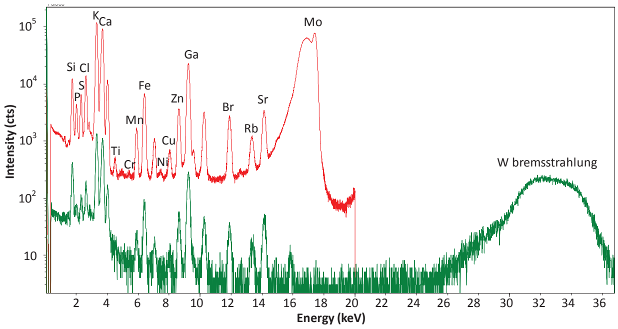

Fig. 1. TXRF raw spectra for the analysis of CMR 1570A sample obtained using Mo and excitation source.

Figure 2 shows the results of the elemental recoveries in the digested samples analysed by means of Mo TXRF. The elemental recoveries ranged from 70 to 110 %. As it can be seen, the lowest recoveries in each sample are obtained for K. This is explained by the fact that K being a light-mid Z element is partially absorbed when measurements are performed in air environment.

In Figure 3 are shown the results for suspended samples. By comparing between the two sample preparation procedures, it can be clearly seen that results are comparable and no significant differences are observed. On this basis, sample suspension being faster and easier compared to digestion is the preferred procedure for vegetal samples.

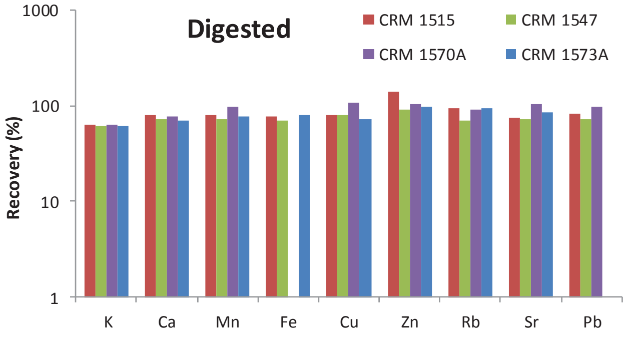

Fig. 2. Elemental recoveries (%) on the digested CRMs.

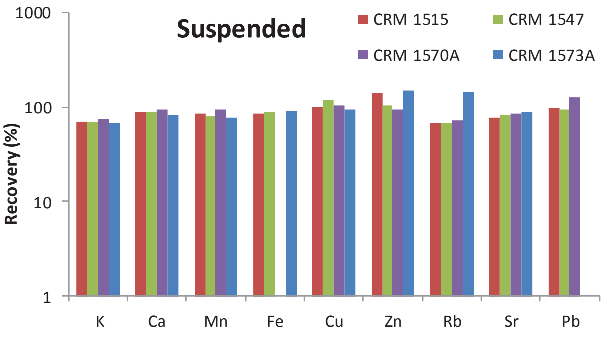

Fig. 3. Elemental recoveries (%) on the suspended CRMs.

3.2. Evaluation of analytical conditions for TXRF measurements of suspensions

Prior to TXRF analysis of all vegetal samples, the following analytical conditions for TXRF measurements were carefully evaluated: internal standardization; sample amount; dispersing agent; sample deposition volume; measurement time; and sonication effect. For this purpose, the CRM 1570A (spinach leaves) was used.

In Figure 4 are shown the results of elemental quantification by using Ga, Rh and Y as internal standards obtained by the W TXRF system. Rh can only be determined by the W system. As it can be clearly seen, there are no significant differences between the three elements used for quantification and consequently Ga was chosen to be used as IS for further TXRF analysis since it can be used in both TXRF systems.

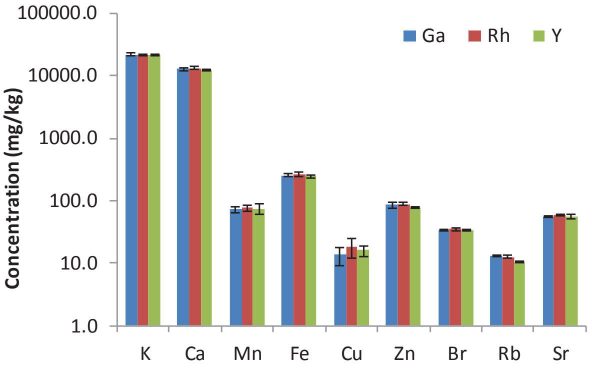

Fig. 4. Elemental concentrations obtained in the analysis of CRM 1570A by using Ga, Rh and Y as internal standards. Error bars represent the standard deviation of duplicate samples.

Table 3 shows the all optimized analytical parameters selected for TXRF analysis of suspended vegetal foodstuff samples.

Table 3. Best analytical parameters for the analysis of suspensions by TXRF.

Analytical parameters	
Internal standard	Ga (10 ppm)
Sample amount	20 mg
Dispersing agent	De-ionized water
Sample deposition volume	10 µL
Measurement time	600 s Mo system, 2000 s W system
Sonication time	5 min

3.3. Analysis of real vegetal samples

After evaluating the accuracy of the method and all the analytical parameters for the analysis of suspensions, 3 real vegetal samples (RM 001 mushrooms, RM 003 strawberries, RM 004 peeled canned tomatoes) were analysed by both TXRF systems to compare the obtained results.

Figure 5 shows the results for the respective studied samples. As clearly observed, for most elements there are no statistically significant differences between results obtained by both TXRF systems and in comparison with the reference values (obtained by ICP-OES).

For sample RM 001, Mn was found in low concentration and it was not detected by the W system due to its limited sensitivity. In sample RM 003, differences are observed for the determination of Cu by the Mo system. This may be attributed to a contamination by external sources. Moreover, inaccurate results were obtained for Rb by the Mo system in sample RM 003. The reason for that may be the very low concentration of Rb in this sample. These differences may be also due to a certain dis-homogeneity of the samples. In sample RM 004 a good agreement between results obtained by both TXRF systems and reference values were obtained.

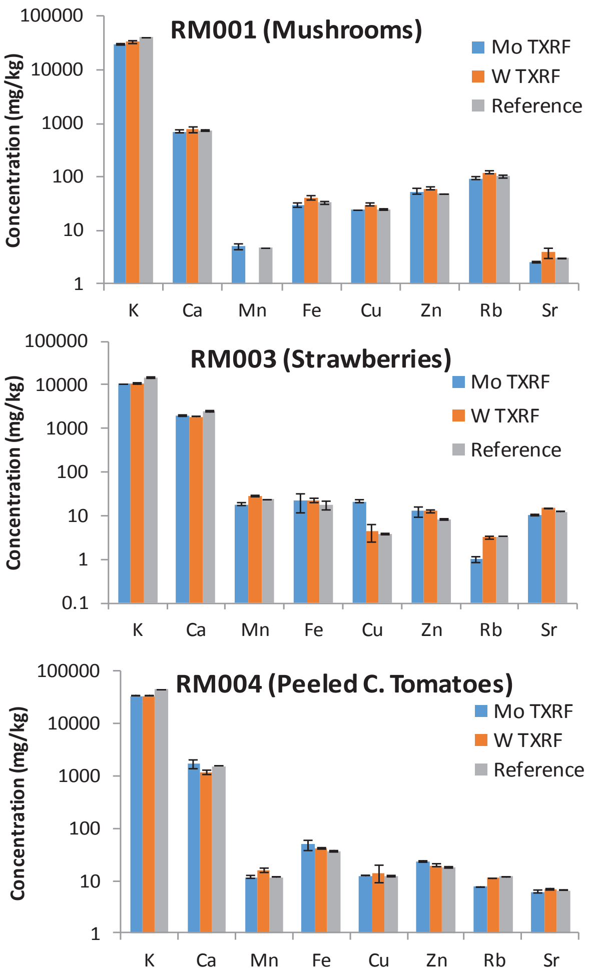

Fig. 5. Comparison of results of three real vegetal samples (RM001 mushrooms, RM003 strawberries, RM004 peeled canned tomatoes) obtained by Mo and W TXRF systems and reference values (measured by ICP-OES). Error bars represent the standard deviation of duplicates.

4. CONCLUSIONS

In this study, we have proposed a fast, easy and reliable method for the analysis of vegetal foodstuffs by means of low-power benchtop TXRF systems.

Suspending the sample in de-ionized water prior to TXRF analysis, showed to be the best option for this kind of samples. In comparison with conventional procedures, such as acid digestion, it is easier and the risk of contamination and analyte losses are lower.

Good agreement was obtained between certified concentration values and those obtained by TXRF. The low sample amount, reagents and consumables since no gas or cooling media are required for operation, makes TXRF a very competitive technique over other TXRF spectroscopic techniques.

In view of the achieved results, sample suspension followed by TXRF analysis can be recommended as a standard procedure for multi elemental analysis of vegetal material.

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