

TXRF spectral information enhanced by multivariate analysis: a new strategy for food and seed traceability

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The rediscovering of regional and local biodiversity in a globalized world together with the improved consumers' awareness about the food quality, safety, provenance and production process, pose food traceability at the center of international laws, standards and agreements

This means that the control institution must be able to answer questions about product authenticity and adulterations, identify the geographical origin of the raw material(s), the transformation cycle and the production site(s), certify the quality of the food in terms of content of high-value metabolites, micro and macronutrients and the absence of potentially toxic compounds and elements. Element profiling is one of the most used strategy for tracing the origin of food and seeds.

Total-reflection X-ray fluorescence (TXRF) spectroscopy is a well-established technique used for the elemental analysis of samples in several scientific fields. Compared to other atomic spectroscopies (ICP-OES, ICP-MS, AAS and XRF), TXRF allows fast analyses of different types of matrixes (water, biological tissues and fluids, minerals, composites, ores, etc.) using a very small amount of sample after a simple sample-preparation. These advantages make the technique very suitable for the analysis of food where reliable and fast analytical methods are crucial to quantify mineral nutrients and potentially toxic elements, to trace the food and to identify frauds. For these purposes, and specifically for food and seed traceability, the detected elements in food are usually quantified (using different approaches which can influence the accuracy of the quantification) and then processed with multivariate statistical analysis. Following this approach, TXRF potentially has the same applicability of other atomic spectroscopies which may show better limits of detection and offer a wider number of quantifiable elements, in particular trace elements. However, compared to other atomic spectroscopies like ICP-OES, ICP-MS and AAS, TXRF gives a continuum spectrum as an output, which can be used, in combination with chemometric approaches, as a fingerprint of the sample. While this approach was already applied on XRF spectra, it has never been applied on TXRF ones. Moreover, to our knowledge, XRF spectra, and in particular TXRF ones, have never been used for food or seed fingerprinting.

For this reason, in the present work we developed, tested and validated a new method for food and seed fingerprinting and traceability using TXRF spectra. In order to fulfill this goal, a group of 24 different genotypes of beans (*Phaseolus vulgaris* L.) grown in two different places in the same region (Veneto, Italy) but at different altitudes (sea level vs 1000 m a.s.l.) were analyzed. The elemental quantitative data as well as the TXRF signals were processed by unsupervised (principal component analysis – PCA) and supervised multivariate techniques (linear discriminant analysis – LDA; partial