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# A feasibility study of tomato fruit quality assessment and traceability by X-ray fluorescence spectroscopy and statistical analysis

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**Summary.** — X-ray fluorescence (XRF) measurements were performed on dried tomato samples coming from "Pachino district", a geographical area recognized by the European Community with the "Protected Geographical Indication" (PGI) label. The purpose of this study is to establish a protocol for in-situ analysis in order to provide a fast and reliable technique for quality assessment and traceability of PGI products. Experimental data were studied by using Principal Component Analysis. The results show the presence of several characterizing elements, which establish a clear fingerprint pattern associated with the geographical origin of this product. Implications and perspectives in applying XRF analysis in order to disentangle tomato samples coming from different Sicilian geographical areas will be discussed.

## 1. – Introduction

XRF analysis allows identifying and quantifying the characterizing and trace elements in biological and environmental samples. This technique is usually fast and non-destructive, since it is able to determine the elemental composition of the samples in few minutes without damaging the analyzed matrices. In the agri-food sector, it has been applied for different purposes: to monitor the content of pollutant elements in vegetal

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crops grown in contaminated environments [1]; to evaluate the distribution of elements in plants depending on soil fertilization practices [2]; to authenticate foodstuffs by searching peculiar chemical elements related to their territory of origin [3]. Among the available XRF tools, portable and compact instrumentation has been widely employed in the environmental sector, as it has the advantage to be used for direct measurements in the field, performing online measurements at various stages of industrial processing.

In this work, we have established a reliable and fast procedure based on a portable XRF device to investigate on the "fingerprint" pattern identifying the provenance of fresh and dried vegetables. As a first step, the XRF analysis on dried samples allowed improving sensitivity, thus revealing the main tracing elements to be considered in the overall compositional evaluation of fruits. In detail, XRF measurements were performed on tomato fruits (*Lycopersicon esculentum* L.) coming from tomato greenhouses located in the Pachino and Ispica municipalities (south-east of Sicily, Syracuse and Ragusa provinces), which fall within the "Pachino district", recognized by the European Community with the PGI label. The PGI "Pomodoro di Pachino" is one of the most important greenhouse vegetal crops cultivated in Sicily and it has a positive impact on the island economy. A mix of external environmental factors (pedological and microclimatic conditions, cultivation techniques, saltwater irrigation), which are different from the other Sicilian geographical areas specializing in tomato cultivation, affects the nutritional and organoleptic properties of this product, making it flavorful and appealing [4]. Due to the higher commercial value of products with the PGI certification, this label is often subject to counterfeiting. Thus, the authentication of a product, by looking to its elemental composition, which identifies the territory of origin, become extremely important in the fight against food frauds and as a tool for traceability.

The elemental composition analysis for certifying food quality and authenticity by using the XRF technique could represent an effective alternative to other standard chemical-physical techniques, such as atomic spectrometry techniques, as Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In a previous study, the reliability and the accuracy of this technique were validated by performing measurements on different parts of PGI Pachino cherry tomatoes (pulp and skin, pulp, skin and dehydrated powder) belonging to the same lot of production [5]. The results, extensively analyzed by using two different statistical tools (PCA and Cluster Analysis), clearly showed that the samples clustered according with the production lot and that it was possible to disentangle different part of the fruit. Furthermore, the effectiveness of the XRF experimental approach was confirmed by comparing the obtained elemental concentrations with ICP-MS measurements, performed on the same tomato samples.

## 2. – Experimental method

Fourteen samples belonging to three typologies (cherry, plum, miniplum) and to seven cultivars of tomatoes (Paskaleto, Pixel, Mozia, Ciringuito, Rokito, Creativo, Lavico) were analyzed. Samples were harvested at full ripeness stage (fully red skin), as usually occurs for marketing, between September and November 2020, from plants grown on sandy-calcareous soils in unheated glasshouses. They were collected from five farms, three of which were located in Pachino and two in Ispica. XRF measurements were performed by using a Bruker portable spectrometer (Tracer IV-SD) on portions of dried pulp without skin obtained from each tomato sample according to the procedure described by [5]. The drying procedure was performed at a relatively low temperature and for a short time (50 °C for 6 hours) to increase the element concentration per unit mass in the samples,

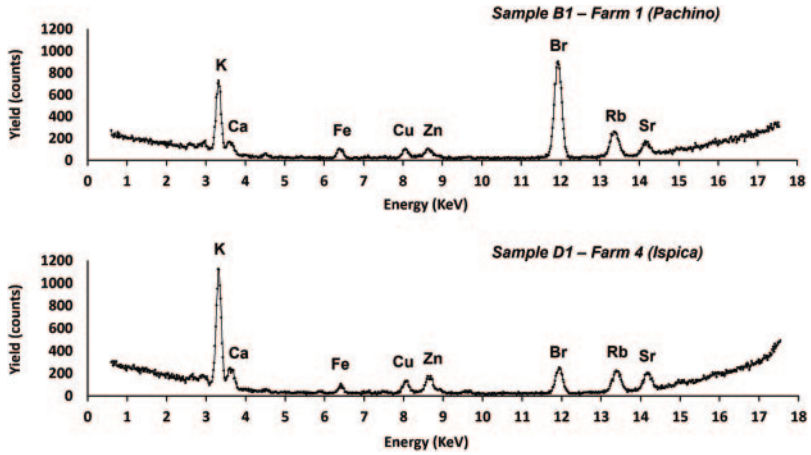


Fig. 1. – XRF elemental profiles of tomato fruits collected in Pachino and Ispica municipalities.

preventing their carbonization. The spectrometer, equipped with an X-ray tube (Rh anode), a collimated beam (3 mm diameter) and a Cu+Al filter, was set to operate at an anodic voltage of 40 keV and a current of 17 $\mu$A. Each sample was irradiated for 300 s [5, 6]. S1PXRF software was used for spectra acquisition, whereas PyMCA software was used for calibration and elemental identification [7]. The methodology used to estimate element concentrations in tomato samples is reported in [5]. Figure 1 shows XRF spectra representing the elemental profile of two tomato samples collected from Pachino and Ispica territory. The highest XRF yields were obtained for K, Ca, Fe, Cu, Zn, Br, Rb and Sr elements. Although some of these elements are macro- and micro-nutrients essential for plant growth, thus falling within the composition of fresh fruits and vegetables [8], their relative yields can be associated with the geographical origin of fruits. Other elements, like Br, may be directly connected to the features of Pachino district and to its proximity to the sea, considered the largest natural reservoir of bromine [9].

## 3. – Statistical analysis

In order to investigate the elemental profile characterizing each sample, the XRF data set was analyzed in the framework of Principal Component Analysis (PCA) [10] by using the MATLAB software package [11]. The input data matrix contains the XRF raw spectra (rows) determined by the fourteen tomato samples coming from Pachino and Ispica growing areas (columns). The selected energy range spans from 0.6 to 17.5 keV. PCA was applied to the standardized matrix. The first three PCs explain 99.4% of the data-set total variability (83.51% - PC1, 15.22% - PC2, 0.66% - PC3). The relatively large PC1 value confirms the data set overall consistency (fig. 2, left side), showing that the fourteen tomato samples have a similar elemental composition, as they came from farms located in a restricted geographical area of Sicily characterized by the same pedo-climatic conditions. On the other hand, PC2 and PC3 make it possible to disentangle tomato samples based on their provenance, as the data set clustered into different groups related to the farms from which they came (fig. 2, right side). This preliminary result suggests that the elemental composition detectable through XRF analysis could be used as a fingerprint to disentangle the PGI "Pomodoro di Pachino" with respect to tomatoes

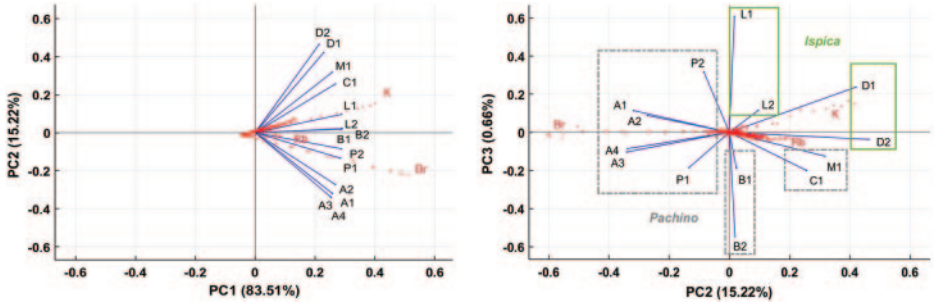


Fig. 2. – PCA biplots obtained by XRF spectra of tomato samples harvested in Pachino. Farm 1: A1, A2, A3 and A4 (cherry cv. Paskaleto) and P1, P2 (plum cv. Pixel). Farm 2: B1, B2 (cherry cv. Mozia). Farm 3: C1 (cherry cv. Ciringuito) and M1 (miniplum cv. Rokito) - and Ispica. Farm 4: D1, D2 (cherry cv. Creativo). Farm 5: L1, L2 (cherry cv. Lavico).

belonging to other geographical areas. Consequently, the performed procedure establishes a solid basis for a wide experimental campaign, to be carried out on samples from other Sicilian geographical areas for investigating this typical product traceability and quality.

## 4. – Conclusions

The XRF technique is a reliable and fast tool to determine the elemental composition of several vegetable crops, representing a viable alternative to standard destructive chemical-physical methodologies. XRF measurements and statistical analysis highlighted the presence of several characterizing elements, which can be associated with the pedoclimatic features and the agricultural practices of the Pachino district affecting tomato plants during their cultivation. Therefore, the obtained elemental signature can be used as a fingerprint to assess the geographical origin and the quality of this product. This will be crucial in order to establish a solid protocol to prevent counterfeiting and to support the traceability system.

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