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A preliminary traceability model for tomato using analysis of stable isotopes, elemental content and chemical markers

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OBJECTIVES:

- To create **a preliminary traceability model** for tomato from different countries (i.e. Slovenia , Italy, Spain and Morocco).
- Three sets of parameters were used: **stable isotopes** of the major bioelements, macro and micro **elements**, and **chemical markers**.

- ***$\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$, $\delta^{18}O$***
- ***P, K, Ca, S, Cl, Zn, Br, Rb, Sr***
- ***total antioxidant potential, total phenolic compounds, ascorbic acid, lutein, nitrates and nitrites, ammonium***

METHODS:

Stable isotope analysis: Simultaneous carbon, nitrogen and sulfur isotopic composition analysis was performed using an element analyser (Elementar vario PYRO cube, OH/CNS Pyrolyser/Element Analyser) linked to a continuous flow isotope ratio mass spectrometer (IsoPrime100; IsoPrime, Cheadle, Hulme, UK). For oxygen, the analysis was carried out using an isotope ratio mass spectrometer (IsoPrime100; IsoPrime, Cheadle, UK) with a multi-flow preparation system (Multi-Flow; IsoPrime, Cheadle, UK).
Elemental analysis: Multi-element determination of the contents of P, S, Cl, K, Ca, Zn, Br, Rb, Sr was performed using non-destructive energy dispersive X-ray fluorescence spectrometry.
Chemical markers analysis:
- ***Carotenoid analysis***: Analysis of lutein was carried out on a HPLC system (Thermo Finnigan, San Jose, USA) with a diode array detector (Thermo Finnigan).
- ***Ascorbic acid analysis:*** Ascorbic acid determination of this extract was performed on a HPLC system (1260 Infinity; Agilent Technologies, Santa Clara, CA, USA) using a diode array detector.
- ***DPPH radical-scavenging activity:*** The AOP of the extracts was determined spectrophotometrically, as the 2,2-diphenyl-1- picrylhydrazyl (DPPH) free-radical-scavenging capacity.
- ***Total phenolics content:*** The TPC was determined according to the Folin-Ciocalteu method described by Singleton and Rossi (1965) [2], with minor modifications.
- ***Ammonium, nitrates and nitrites nitrogen analysis***: The concentrations of ammonium in the extracts were determined according to the EN-ISO 11732 (1997) method, and nitrite and nitrate according to the ISO 13395 (1996) standard.

RESULTS:

Table 1: Stable isotope and elemental compositions for the tomato samples from the different countries of origin.

Country of origin	Isotope ratio (mean ±SD; ‰)				Element analysis (mean ±SD)								
	$\delta^{13}C$	$\delta^{15}N$	$\delta^{18}O$	$\delta^{34}S$	Ca (g/kg)	P (g/kg)	K (g/kg)	Cl (g/kg)	S (g/kg)	Zn (mg/kg)	Br (mg/kg)	Rb (mg/kg)	Sr (mg/kg)
Slovenia	-27.4 ±0.6	4.0 ±3.2	-3.6 ±0.8	1.9 ±3.6	1.75 ±0.82	5.16^{a} ±0.69	42.9 ±2.39	6.87 ±1.79	1.85 ±0.58	15.8 ±3.88	13.3 ±9.95	18.6 ±0.96	9.57 ±9.17
Italy	-27.6 ±1.1	2.7 ±3.2	-1.2 ±1.2	3.8 ±3.2	2.12 ±1.01	3.72^{b} ±0.98	36.45 ± 8.80	5.52 ±1.38	2.05 ±0.48	18.7 ±4.71	38.3 ±36.86	6.16 ±0.97	7.07 ±5.10
Spain	-26.6 ±0.7	3.4 ±2.9	-2.2 ±0.4	3.5 ±1.9	1.65 ±0.42	3.61^{b} ±0.68	33.7 ±5.98	5.28 ±2.18	1.75 ±0.26	14.2 ±3.55	16.3 ±6.95	9.79 ±5.34	17.45 ±8.18
Morocco	-27.3 ±0.9	5.7 ±3.3	-1.2 ±2.9	4.3 ±4.0	1.79 ±0.21	4.20^{ab} ±0.56	35.3 ±4.13	6.10 ±1.53	1.66 ±0.11	14.18 ±2.38	20.6 ±7.07	6.46 ±2.06	10.2 ±3.25
ANOVA*						0.0182							
KW test**			0.0078									0.0130	0.0367

*Different letters (a,b,c) in the same column indicate statistically significant differences ($p < 0.05$). (Duncan's tests). Only p-values lower than 0.05 are reported.
**According to KW test only p-values lower than 0.05 are reported.

Table 2: Chemical markers for the tomato samples from the different countries of origin.

Country of origin	Chemical markers (mean ± SD)					
	AOP (mmol DPPH/ 100 g F.W.)	TPC (mg/ 100 g F.W.)	AA (mg/ 100 g F.W.)	Lutein (mg/ 100 g F.W.)	Ammonium (mg/ 100 g D.W.)	Nitrates (mg/ 100 g D.W.)
Slovenia	0.13 ±0.04	33.9 ±8.14	19.5 ±5.93	0.19 ±0.36	14.5 ±2.37	6.70 ±6.06
Italy	0.12 ±0.06	40.3 ±13.9	22.7 ±9.36	0.38 ±0.32	15.3 ±6.45	10.5 ±12.6
Spain	0.09 ±0.05	32.7 ±11.5	16.2 ±6.19	0.35 ±0.19	14.5 ±2.37	6.70 ±6.06
Morocco	0.08 ±0.01	25.5 ±2.88	14.0 ±2.93	0.43 ±0.40	19.0 ±5.23	15.8 ±10.0

*None of parameters was subjected to ANOVA due to not being normally distributed and homoscedastic. According to Kruskal- Wallis test none of parameters was statistically significant.
AOP, antioxidant potential; TPC, total phenolics content; AA, ascorbic acid

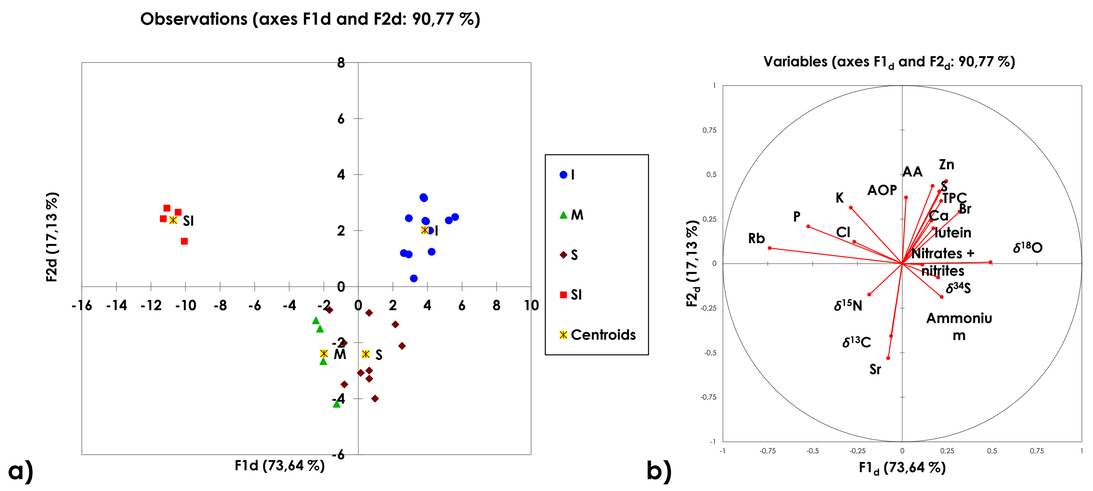

Figure 1. Combined stable isotope, elemental and physical-chemical analysis. **(a)** Discriminant score plots of the 30 tomato samples originating from Slovenia (SI; n = 4), Italy (I; n = 12), Spain (S; n = 10) and Morocco (M; n= 4). **(b)** Plot of the correlations between the initial variables and the discriminant factors, here as $F1_d$ and $F2_d$.
AOP, antioxidant potential; TPC, total phenolics content; AA, ascorbic acid.

- **Overall prediction ability: 80.0%**
- **The most influential parameters:**
  - F1: Zn, P, ascorbic acid
  - F2: ascorbic acid, Ca, Rb

CONCLUSIONS:

- In conclusion, this study provides the **first evaluation** of the use of **stable isotope** and **elemental parameters** in combination with **chemical markers** to define an initial traceability model for commercial tomato samples.

FURTHER RESEARCH: Enlargement of the number of authentic samples, obtained over a number of years and creation of reliable **traceability models.**
Drawback: expanded databases require more complex interpretations due to increased number of samples and their natural variations.

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