Determination of mineral and trace elements in leaves of four fruit trees (Argan, Olive, Carob and Almond tree) by inductively coupled plasma optical emission spectrometer

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ABSTRACT
Eleven minerals (Zn, Cu, B, Ca, K, Mn, Mg, Fe, P, S, and Na) were determined in leaves of Moroccan fruit trees such as argan tree, olives tree, carob tree and an almond tree. Dry digestion procedure and acid digestion for total concentration were used. Al mineral elements were determined by inductively coupled plasma optical emission spectrometer (ICP-OES). The obtained results show that the compositions of the four trees are divided into two main classes. The first class contains sample Argan leaves. The second class has two subclasses, one containing sample Carob leaves and the other containing olive leaves and almond leaves.

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1. Introduction:
In recent decades, the Moroccan State has paid particular attention to agriculture, given its important and diverse roles; agriculture contributes significantly to reducing poverty and creating employment (about 50% of the population), preserving the environment, social stability, economic growth and food security. The contribution of agriculture to national gross domestic product is estimated at 15% and to exports at 10% [1]. Fruit trees are a major pillar of agriculture in Morocco and are a vital part of the state’s strategies to improve yields and increase competitiveness. This situation has made this area a major focus of research to achieve the objectives set. This is achieved by improving crop management or plantation renewal techniques and extending the area planted. This study focuses on four fruit trees: Argan, almond, olive and carob. The choice of these trees is dictated by their importance in terms of quantities produced, occupied spaces and values generated and their similarities in terms of morphology, constituents and fruits. The fruits of the argan tree, the almond tree and the olive tree have the same, is mainly made of two parts, the pulp (mesocarp) which is covered by skin (epicarp), and the kernel (endocarp).

The argan tree [Argania Spinosa (L).Skeels (Sapotaceae)] is an endemic species in southwestern Morocco [2]. The argan tree area is approximately 800,000 hectares [3]. The argan tree grows wild and abundantly in the arid and semi-arid areas of south-western Morocco and is the country’s second-largest forest species. From an economic point of view, arganerie sustains about 3 million people, including 2.2 million in rural areas and provides more than 20 million working days [4].

The economic value of the argan tree increases every day because of the derivatives produced; argan oil is the most expensive and useful derivative of the argan tree given its exceptional organoleptic and nutritional qualities. The composition of this part is well documented [5-10].

The olive tree (Olea europaea L.) is a characteristic tree of the Mediterranean region, giving a typical aspect to the diet of this region. The olive tree is the main fruit species cultivated in Morocco [11]. The overall value generated by this sector represents 5% of national gross domestic product [12]. These figures make the olive sector an important pillar of agriculture...
in Morocco. Olives are among the most exported agricultural products (the world’s second-largest exporter of olives and the sixth-largest exporter of olive oil). The almond tree is the second fruit species in Morocco after the olive tree; it occupies an area of 128000 hectares and constitutes a population of about 16 million trees [13]. Marked by a good adaptation to drought and a remarkable resistance to winter cold, the almond tree is located mainly in the mountains, the Rif, the piedmont of the High Atlas and in the southern areas with an arid or semi-arid climate. In terms of production, Morocco ranks fifth among the producing countries, behind the USA (220,000 t), Spain (70,000 t), Greece (16,000 t) and Italy (14,000 t). Production is insufficient due to the area occupied, efforts are underway to optimize production and strengthen the place of culture [13]. From a nutritional point of view the almond tree constitutes a source of proteins and lipids, carbohydrates, mineral elements and antioxidants [14-16] and α-Tocopherol [17]. The carob tree [((Ceratonia siliqua L): (cesalpinaceae)] has long been growing in most Mediterranean countries: Spain, Italy, Greece, Turkey, Algeria, Cyprus and some other countries. World production is about 310000 T/Year. Spain is the world’s largest producer of carob. In Morocco the carob tree is found in several places: occidental and oriental Rif, Gharb, Saiss, Anti-Atlas and central plateau [18]. Morocco is the fourth producer after Spain, Italy and Portugal with production reached 84000 T/Year [19]. The carob tree begins to produce pods from the age of 6 years. Production gradually increases with age and stabilizes between 40 and 50 years of age, reaching 100 to 200 kg/tree [20]. Carob pod provides two important derivatives: Carob kernels and Carob kibbles. Carob is mainly used is food industry as raw material and also as animal feed [21].

The objectives of current research is to determine the mineral composition of the leaves of four fruit trees: the argan tree, the almond tree, the olive tree and the carob tree and make a comparison between them; in the overall objective to contribute to the determination of a rational nutrition for these four trees based on the foliar diagnosis.

2. Material and methods:
2.1 Sampling:
The samples analyzed in this study were obtained in the same region and at the same time. The trees have not undergone any phytosanitary or nutritional treatment.
2.2 Chemicals:
Single standard solution of 1000 µg/ml of nine elements (K, Ca, Cu, Na, Fe, B, Zn, Mn, Mg) dissolved in 2% wt HNO3 supplied by Merck Millipore (Darmstadt, Germany) were used as a stock solution for calibration. Nitric acid and chlorhydric acid were reagent grade solvents. Ultrapure water with Maximum resistivity of 18.2 MΩ/cm, obtained from a Milli-Q Millipore system (Darmstadt, Germany). Argon Alpha-gas (purity higher than 99.995) supplied by Air liquid was used.
2.3 Apparatus:
The Analysis was carried out using a Perkin Elmer Model Optima 8000 DV spectrometer, equipped with an autosampler ASX-520 supplied by Teledyne CETAC Technologies (Omaha, USA) and a charge-coupled device (CCD) detector. The Gem Tip, Cross-Flow II nebulizer coupled with the scott-chamber was used as a sample introduction system.
2.4 Preparation of sample:
One gram of sample was weighed and dried at 80°C for 2h into porcelain crucible, then charring in a muffle furnace for 2h at 500°C. After cooling 10 drops of water were added to wet ash, then 4 ml HNO3 were added and the excess of nitric acid was evaporated on a hot plate at 120°C. Then crucible was returned to the furnace for 1H at 500°C. Finally, the ashes were dissolved in 10 ml HCL [22].
2.5 Determination
The operating conditions of the ICP-OES equipment during this study were set as follow; 14 L min⁻¹ of plasma gas flow rate, 0.2 L min⁻¹ of auxiliary gas flow rate, 0.8 L min⁻¹ nebulizer gas flow rate, 1300W of RF power 1.3 ml min⁻¹ of sample flow rate with a time flush of 7s. All the elements were detected in axial mode. The wavelength used for the quantification were: zinc 213.857 nm, copper 324.752 nm, iron 239.562 nm, potassium 766.490 nm, magnesium 285.213 nm, Boron 249.772 , sodium589.592 nm, manganese257.61 and calcium 317.933 nm.

3. Results and discussion:
For years the foliar diagnosis has been based as an interesting approach to the determination of nutritional compounds in trees to know the causes of nutritional disorders, forest wasting [23], and fluctuations in crop yields. The foliar analysis is used in this study to determine the mineral composition of four fruit trees in Morocco to determine the similarities and differences of their composition to study the possibility of similarities in the nutrition needs of these trees. The obtained results in this study are summarized in table 1.
**Table 1. Content of elements (mg.kg⁻¹) in four trees leaves.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>λ (nm)</th>
<th>Olive leaves</th>
<th>Carob leaves</th>
<th>Almond leaves</th>
<th>Argan leaves</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>766.49</td>
<td>10220±817</td>
<td>5097±407.76</td>
<td>8122±649</td>
<td>4092.30±327</td>
</tr>
<tr>
<td>Ca</td>
<td>317.933</td>
<td>28580±2286</td>
<td>16400±1312</td>
<td>26457±2116</td>
<td>21051±1684</td>
</tr>
<tr>
<td>Mg</td>
<td>285.213</td>
<td>3165±253</td>
<td>2708±216.64</td>
<td>5845±467</td>
<td>5621.90±449</td>
</tr>
<tr>
<td>P</td>
<td>213.617</td>
<td>761.8±60</td>
<td>89.8±7.18</td>
<td>611±48.88</td>
<td>525.50±42</td>
</tr>
<tr>
<td>S</td>
<td>181.975</td>
<td>791.6±63</td>
<td>30.6±2.44</td>
<td>1253.07±100</td>
<td>1182.63±94</td>
</tr>
<tr>
<td>Na</td>
<td>589.592</td>
<td>337±26</td>
<td>275.7±22.05</td>
<td>1658±132</td>
<td>6381.24±510</td>
</tr>
<tr>
<td>B</td>
<td>249.772</td>
<td>23.9±1.91</td>
<td>51±4.08</td>
<td>29.50±2.36</td>
<td>123.30±9.86</td>
</tr>
<tr>
<td>Fe</td>
<td>239.562</td>
<td>372.9±29.83</td>
<td>183±14.64</td>
<td>393.70±31</td>
<td>1283±102</td>
</tr>
<tr>
<td>Cu</td>
<td>324.752</td>
<td>5.8±0.46</td>
<td>2.90±0.23</td>
<td>2.88±0.23</td>
<td>12.77±1.02</td>
</tr>
<tr>
<td>Zn</td>
<td>213.857</td>
<td>19.8±1.58</td>
<td>7.60±0.60</td>
<td>9.50±0.76</td>
<td>15±1.2</td>
</tr>
<tr>
<td>Mn</td>
<td>257.61</td>
<td>61.1±4.88</td>
<td>25.70±2.05</td>
<td>34.40±2.75</td>
<td>51±4.08</td>
</tr>
</tbody>
</table>

For the argan leaves, our results are less than those reported in an independent study for K, Ca, Zn and P, and higher for Mg and Cu [24]. To interpret our results we decided to use the Principal Component Analysis (PCA).

![Figure 1. Circle of correlation of mineral elements.](image)

Dimensions 1 and 2 showed 47.63% and 38.54%, respectively, of the variability between the varieties whose sum of the variance is 86.17% (Figure-1). Examination of the correlations of the variables shows that the variables "Mg, Cu, Fe, Na and B" are inversely positively correlated with axis 1 with values of the correlation coefficient equal to (+0.58; +0.93; +0.95; +0.82 and 0.57) respectively. For the variables "S, Mn, Zn, and P", they are positively correlated with axis 1 with correlation coefficient values equal to (+0.78; +0.56; +0.48; +0.41 and +0.42) respectively. For the variable "Ca", it is positively correlated with axis 2 with a value of the correlation coefficient (+0.97). For variable "K", it is positively correlated with axis 2 with a value almost equal to (+0.99). Figure 2 gives a graphical representation of the trees studied (olive tree, almond tree, argan tree, carob tree). We noticed that the argan tree leaves have the highest values of B, Na, Fe Cu and Mg compared to other trees. While the leaves of the two trees (olive and almond) have the highest P and Ca values. For the parameters “Ca, P, Zn, Mn and S are low in the carob leaf samples.
The hierarchical classification of leaves trees by analytical results is presented in Figures 3 and 4. The dendrogram of the hierarchical bottom-up classification shows that the 4 samples are divided into two main classes which are found on the factorial plane of axes 1 and 2 of the ACP. The first class contains sample 4 (Argan leaves). The second class has two subclasses, one containing sample 2 (Carob) and the other containing the two samples 1 and 3 (olive leaves and almond leaves). Then the results of the hierarchical classification classified our samples into three groups according to their leaves mineral element content:

- **1st** group: Argan tree leaves.
- **2nd** group: Carob tree leaves.
- **3rd** group: Almond and olive trees leaves.
4. Conclusion:
This study allowed us to highlight eleven minerals content of the leaves of four fruit trees. The results obtained in this work show that the argan tree leaves have the highest values of B, Na, Fe Cu and Mg compared to other trees. While the leaves of the two trees (olive and almond) have the highest P and Ca values. For the parameters “Ca, P, Zn, Mn and S” are low in the carob leaf samples. It is also important to mention that the four samples of leaves are divided into two main classes according to their compositions. The first class contains Argan leaves. The second class has two subclasses, one containing Carob leaves and the second containing the olive leaves and almond leaves.

References:


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