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Thermal analysis and determination of the heavy metal content of the plant *Urtica Dioica* L. by atomic absorption spectroscopy

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Abstract: Today, medicinal plants are still the primary reservoir of new drugs. They are considered an essential source of raw material for the discovery of new molecules needed for the development of future remedies. Among these plants, we find *Urtica dioica* L., which belongs to the Urticaceae family. It is a perennial herbaceous plant commonly known as "nettle" it has been reported to have various pharmacological activities like antibacterial, antioxidant, analgesic, anti-inflammatory, antiviral, and anticancer effects. In the present work, we are interested in one hand, in valuing this plant which was harvested from the region of Meknes, by thermal and gravimetric analysis ATD/ATG to determine the loss of mass as a function of temperature. This phenomenon was confirmed by the calcination technique in a muffle furnace at different temperatures (110°C and 300°C, 600°C). on the other hand, after the calcination of the plants, detection of the heavy metal content by an atomic absorption spectroscopy (AAS) technique was performed. The results obtained showed simultaneously high concentrations of Ca, K, Na, Li, and Cd and low concentrations of Pb, Ni, Cu, and Zn.

Keywords: *Urtica dioica* L.; ATD / ATG; Heavy metals; SAA

1. Introduction

Urtica dioica L. of the Urticaceae family is a perennial herb known as nettle. Is widespread in Morocco (Bnouham *et al.*, 2003). The plant *Urtica dioica* L. is derived from the word "Uro" meaning burning or "urere" meaning to prick (Bourgeois *et al.*, 2016). It is an annual herbaceous plant of 0.6-1.2 m in height with spines and erect stems. It is quadrilateral in shape, the opposite leaves have teeth or fissures, and each node has two or four states (Ghedira *et al.*, 2009). In general, the leaves and underlying base of the nettle plant are used internally as blood products. Blood purifiers, menstrual agents, diabetes, antiseptic, nasal and menstrual drainage, stiffness, skin inflammation, iron deficiency, nephritis, and hematuria. It is also used to treat jaundice, menorrhagia, and diarrhea (Joshi *et al.*, 2014). As well as the aqueous extract of nettle exerts a hypotensive effect in the rat in vivo (Legssyer *et al.*, 2002). The plant *Urtica dioica* L. contains distinct classes of natural restorative mixtures, including phytosterols, saponins, flavonoids, tannins, sterols, fatty acids, carotenoids, chlorophylls, proteins, amino acids, and vitamins. It is a very nutritious plant, easy to digest, and rich in minerals (especially iron), vitamin C and pro-vitamin A (Said *et al.*, 2015). In Morocco, these medical and nutritional data remain poorly explored, and the applications of nettle are being increasingly neglected both in the culinary field and in the medical and veterinary areas (Dhouibi *et al.*, 2020).

Most plants contain trace nutrients. Some of these heavy metals may exist as traces which will have a negative impact on the environment (Moreira *et al.*, 2020). The best known for their dangerousness are lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn). We must add to this list Arsenic (As) and selenium (Se).

Due to the high density of some toxic metals, many authors have become accustomed to using the term "toxic metals" instead of heavy metals, since for decades, there has been a widespread opinion confusing heavy metal. With toxic metals. But today, it is clear that some heavy metals are not only non-toxic, but only a small amount have a significant effect on the metabolism of living organisms (Dikilitas *et al.*, 2016), (Chojnacka and Mikulewicz, 2014), (Zhuang, 2019). On the other hand, some lighter metals, such as beryllium with a specific gravity of 1.85 have a high toxicity (Malayeri, 1995). The ecotoxicological risk of metal contamination in non-agricultural terrestrial environments generally follows the path from soil to plant, then to animals and humans (Remon, 2006). The trace metals elements are not degradable by natural chemical or biological processes; hence, their accumulation persists in the environment for long periods (Andaloussi *et al.*, 2021).

For this, it is interesting to study the plant *Urtica dioica* L using infrared spectroscopy, thermodifferential and thermogravimetric analyzes (ATD/ATG) to highlight the losses their loss of mass and the determination of all the functions of the molecules present in said plant. On the other hand, determine its heavy metal content by using the atomic absorption spectrophotometer (AAS).

2. Materials and methods

2.1. Harvesting of plant material

The city of Meknes (33 ° 53'36 N / 5 ° 32'50 W) is famous for its subtropical climate. For this reason, nettles live freely in all corners of the city. The harvest ended in February. Drying is carried out for 15 days in a dry and dark place (**Figure 1**).

2.2. Thermogravimetric and thermodifferential analysis

Thermogravimetric analysis is a type of thermal analysis that measures the change in mass of the sample over time at a given temperature or temperature curve. The purpose of the thermal differential analysis is to follow the evolution of the temperature difference between the study sample and the control sample. For this, 5 mg of plant powder is introduced into an aluminum crucible for thermal analysis. The device used is a Shimadzu 60 type which simultaneously executes DTA/TGA.

Figure 1. The *Urtica dioica* L. plant

2.3. *Infrared spectroscopy*

The identification and determination of the chemical functions present in *Urtica dioica* L. have been reported by infrared spectroscopic technique. The absorption bands are expressed in cm^{-1}.

2.4. *Calcination*

During the heating process, a variety of chemical reactions take place causing. the material to change and decompose. The calcination is carried out in a muffle furnace at different temperatures: 110°C, 350°C, and 600°C.

2.5. *Atomic absorption spectroscopy (AAS)*

After calcination of the plant at 600°C, the ash obtained is treated by mineralization with concentrated nitric acid and then filtered on Whatman 0.45µm paper to obtain a ready-to-use solution for the determination of the concentration. Heavy metals by atomic absorption spectrometry.

3. Results and discussion

After harvesting the plant of *Urtica dioica* L.. The dried and ground, a preliminary analysis was carried out of the latter by infrared spectroscopy of Fourier transform in order to determine all the functions present in the molecules contained in this plant. To do this. 10 mg of the powder of the plant of *Urtica dioica* L. The was ground in the presence of 100 mg of KBr using an agate mortar. The powder thus obtained was analyzed by infrared spectroscopy. The IR spectrum of the raw *Urtica dioica* powder shows the presence of an intense and wide band around 3500 cm^{-1}corresponding to the vibration band (OH) of the acid function, and another band which appears around 2900 cm^{-1} attributable to the tetragonal valence (CH) vibration band. Likewise, we note the presence of a thin band around 1700 cm^{-1} relating to the valence vibration band of (C = O) of the acid function. From these it can be assumed that the powder contains organic molecules containing an acid function (**Figure 2**). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using an analyzer supplied by DTA 60, at a temperature of 25°C up to 600°C and a heating rate of 20° /min. Thermal degradation of the sample can be identified by the decrease in its weight. The difference in mass is due to the endothermic and exothermic combustion reactions that occur, the transformation process is characterized by thermal degradation presented by 3 stages, the initial weight loss (-13.302%, -2.719 mg) observed at 110°C is attributed to the evaporation of the water contained in the plant.

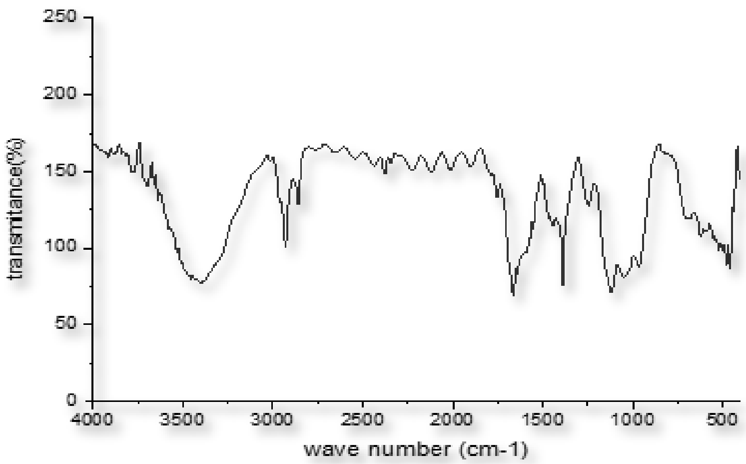

Figure 2. IR spectrum of raw *Urtica dioica* L. powder

The second step is observed at T = 325°C corresponds to the start of thermal degradation of the organic material with a mass loss of (-35.127%, - 7.180 mg). The third step, located at a temperature of 600°C, records

a loss of mass of (-20.117%, - 4.112 mg) corresponding to the total loss of organic matter. The ATD diagram of the plant shows peaks indicating the different degradation reactions. An endothermic peak at 70.62°C is attributed to the evaporation of the absorbed water and two exothermic peaks at 324.71°C and 458.48°C is attributed to the degradation of organic matter (**Figure 3**). To explain this loss of mass, the sample, was calcined in a muffle furnace at different temperatures: 110°C, 350°C and 600°C, then analyzed by IR spectroscopy. The results of this calcination are presented in the following **Table 2**.

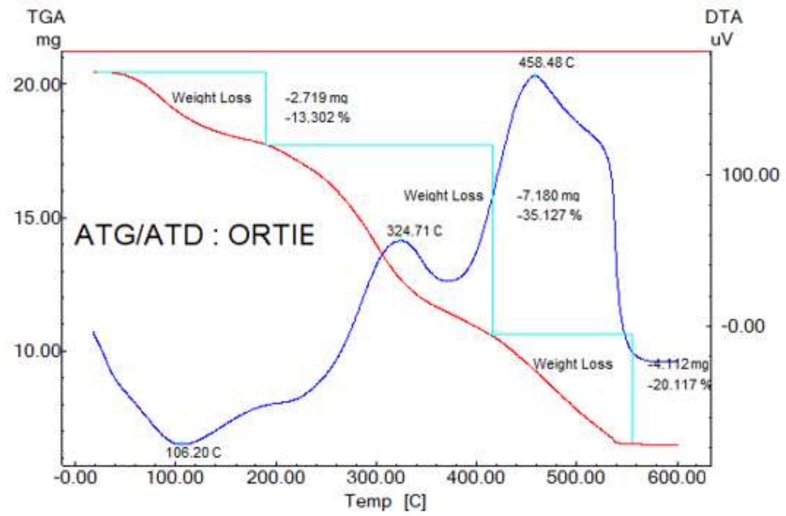

Figure 3. ATD / ATG curve of the raw powder of *Urtica dioica* L. leaves

Table 2. Loss of mass of *Urtica Dioica* L. during calcination

Temperature	M_i (g)	M_f (g)	A loss of mass (%)
110	10	7.955	20.45
350	10	3.944	60.56
600	10	2.605	73.95

The two results from the ATD/ATG and the calcination clearly show that at a temperature of 600°C, the plant has lost a variant mass between 68.55% and 73.95%. The rest of the plant is mineral matter. At the same time, the masses obtained were analyzed by infrared spectroscopy. The infrared spectra of the compounds taken at temperatures 110°C, 350°C and 600°C are presented in **Figure 4**.

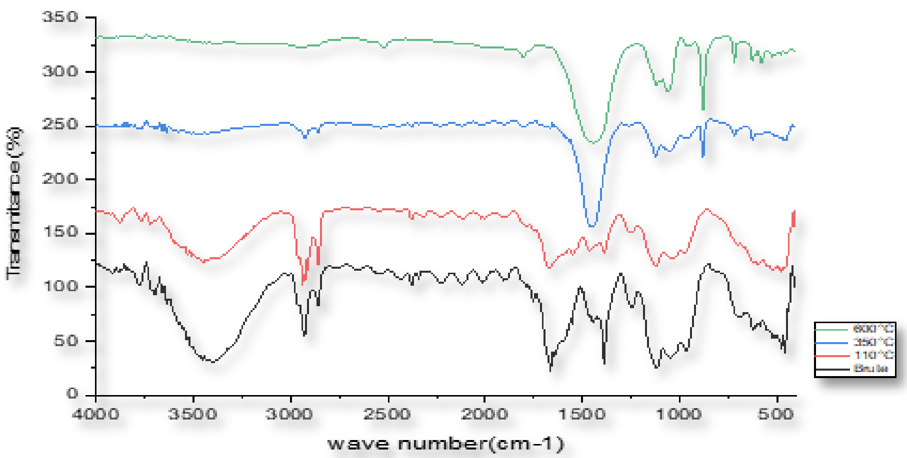

Figure 4. IR spectrum of *Urtica dioica* at various temperatures

On the infrared spectrum of the plant calcined at 110°C, a decrease of the OH band is recorded. That is due to the evaporation of water molecules in the plant. While for a temperature of 350°C, the IR spectrum shows the disappearance of the valence vibrational band (OH).And the decrease of the vibration band of the CH function around 2900 cm^{-1}. That means the partial disappearance of organic matter. For the infrared spectrum of the plant calcined at 600°C, we record the total disappearance of organic matter. And we observe the appearance of a new band around 1078 cm^{-1} which can be attributed to the vibration band Si-O of silica, and other band around 874 cm^{-1} which may correspond to quartz. The band at1460 cm^{-1} and a band at 712 cm^{-1} are respectively characteristic of the vibrations of the CO function of calcium carbonate. A band around 3688 cm^{-1} is attributed to the vibration of the OH bond of the hydroxyl groups of kaolinite (Fliou *et al.*, 2019) (**Figure 5**).

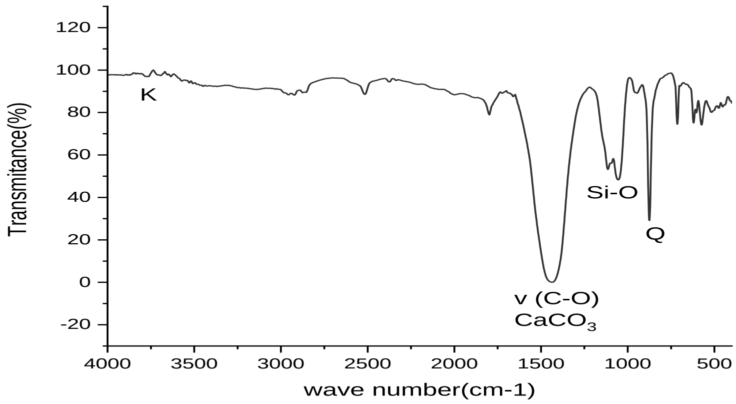

Figure 5. IR spectrum of *Urtica dioica* L. at 600°C (K: Kaolinite, $CaCO_3$: Calcinite, Q: Quartz, SiO: Silica)

3.1. Determination of heavy metal content by atomic absorption spectrophotometry

The objective of this work is to show whether the plant had toxic trace elements or not. For this the plant of *Urtica dioica* L., which was calcined at a temperature of 600°C is again mineralized in the presence of nitric acid. The filtrate obtained is analyzed by atomic absorption spectrophotometry. The heavy metal content results are summarized in **Table 3**.

Table 3. The heavy metal content of *Urtica dioica* L.

Metals	Contains in the plant (µg / g)	Contents normal inplants by WHO (µg/g) (Riffi *et al.*, 2020)	The heavy metal content of the human body (µg/g) (Fliou *et al.*, 2020)
Ca	2590.00	-	19000.00
K	1070.00	-	-
Li	500.00	-	-
Cd	42.60	0.30	-
Na	36.80	-	800.00
Fe	13.10	-	60.00
Zn	2.90	-	33.00
Cu	1.20	150.00	1.00
Ni	0.21	-	0.02
Pb	0.14	10.00	-

The atomic absorption results obtained revealed high levels of Ca and K with high levels of 2590µg/g and 1070µg/g in *Urtica dioica*. In plants, heavy metals (Cu, Zn, Ni, Fe, Co) are essential for major physiological

processes, in particular respiration, photosynthesis, or the assimilation of macronutrients (Jadia and Fulekar, 2009). And very low Pd and Cu contents in *Urtica dioica*, respectively 0.14µg/g and1.20µg/g. The limit concentration in vegetable raw materials is provided by the World Health Organization in accordance with the "Regulation Review" of various countries the current standards are respectively lead 10µg/get copper 150 µg/g (Kabata-Pendias and Pendias, 2001). Regarding the Zinc content, the results showed that *Urtica dioica* had a very low concentration (2.90µg/g) compared to the literature or Sathiyamoorthy et al reported that Zinc was more concentrated in *Populuse uphratica* at 113 µg/g and in *Achillea fragrantissima* at 85 µg/g (Sathiyamoorth *et al.*, 1997). The results have also shown that the Fe content in *Urtica dioica* is of the order of 13, 10µg/g. The latter is higher compared to the contents found by Smati et al where the maximum iron concentration is 2.4µg/g at the leaf level and 2.16µg/g at the level of the *Zygophyl lumgeslini* fruit (Smati *et al.*, 2011). The Cd content obtained in *Urtica dioica* L. was 42.60µg/g, a very high value compared to the WHO tolerance limit (0.3 µg/g). This could probably be explained by soil pollution in the region where it was picked. In addition, Zn and Cd are the most mobile trace metals in soils compared to other elements such as Pb and Cu (Rafiq *et al.*, 2022).

Conclusion

In this work, a study was conducted to analyze the powder of the aromatic and medicinal plant *Urtica Dioica* L. from the region of Meknes by ATD and ATG to determine the loss of mass as a function of temperature. This phenomenon was confirmed by the technique of calcination at different temperatures (110°C, 300°C, 600°C). The remaining residue was used to determine the heavy metal content of the plant *Urtica Dioica* L. by atomic absorption spectrophotometry (AAS) analysis. The results obtained showed that the plant had high levels of Ca and K, which can be considered as plant nutrients, and low levels of Pb, Cu and Zn.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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