



Authenticity Pattern of Commercialized *Emblica officinalis* Using Thermal Decomposition and Elemental Studies

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Abstract: Tremendous raise up on medicinal plants in global market, the marketers are focusing to improve their turnover and hence the feasibility of adulteration using similar physiological and/or chemical propertied materials are being increased. To overcome these quality issues on *Emblica officinalis* based herbal samples, the present investigation carried out to study thermal decomposition nature and elemental compositions of its genuine sample and market available commercial samples. The TGA-DTA studies provided significant differences in the decomposition percentage of phytochemicals as 28.4% and 21.5% for genuine (AMGS) and market (AMMS) samples respectively. It implies that the beneficial components of *E. officinalis* are declined while commercialization of this herbal. Also the mineral compositional studies using EDAX and ICP-OES opened the micro nutritive elements shortages in commercial samples while comparing the genuine. The obtained results strongly evidenced that these decomposition and elemental studies can be helpful to scrutinize the certainty of *E. officinalis* samples and may other herbals too.

Keywords: *Emblica officinalis*, Herbal Genuineness, Thermogravimetry, Mineral Compositions

1. Introduction

Recently utilization of ecofriendly and bio friendly herbal products for the prevention and remedial of human diseases is on the flow in the wake of its less side effects and easily available at affordable costs. This global trend “Return to nature” makes the herbal industry as one of the fast growing sector in the International market. India, with its rich biodiversity and traditional knowledge in medicinal systems has a tremendous potential and advantage for supplying the herbal products in the global market [1, 2]. Standardization of herbal products with proper scientific techniques is the prerequisite one to get its authenticity, uniformity, safety and efficacy preventing from adulterations if any for the trade and commerce.

Emblica officinalis, a member of Euphorbiaceae family, is commonly known as Amla and Indian Gooseberry. Being one of the prioritized medicinal plants in India, the annual consumption and growth rate of it are estimated as 10,000

tonnes and 22.5% respectively with reference to the trade [3]. This species is native to India and widely distributed in tropical and subtropical regions including Pakistan, Uzbekistan, Srilanka, South East Asia, China, Malaysia, and Indonesia. It is an important medicinal herb used in Indian traditional medicinal systems like Ayurveda and Unani as well as in Chinese herbal medicine and Tibetan medicine [4]. *E. officinalis* fruits are spherical of about 1.5-2.5 cm in diameter, globose, fleshy, pale yellow with six obscure vertical furrows enclosing six trigonous seeds in two seeded three crustaceous cocci [5]. The skin is thin, translucent and adherent to the very crisp, juicy, concolorous flesh [6]⁷. Its fruits are highly nutritious and one of the richest sources of vitamin-C. It contains several chemical constituents like amino acids, minerals, tannins like Emblicanin A and B, alkaloids and phenolic compounds [7, 8]. The green fruits are made into pickles and preserves to stimulate the appetite. It is often used in the form of Triphla which is an herbal formulation containing fruits of *Emblica Officinalis*,

Terminalia chebula and *Terminalia belerica* in equal proportions [9]. It has long been used to treat a broad spectrum of disorders including anorexia, indigestion, and anemia [10]. Pharmacological research reports on *E. officinalis* reveals its analgesic [11], anti-tussive [12], anti-atherogenic [13], adaptogenic [14], cardio [15], gastro [16], nephron [17], neuro protective [18] and anticancer [19] properties. EO is also reported to possess chemopreventive [20], radio [21], chemo [22] and immunomodulatory [23], free radical scavenging [24], antioxidant [25], anti-inflammatory and anti-mutagenic activities [26]. These properties are efficacious in the prevention and treatment of various diseases like cancer, atherosclerosis, diabetes, peptic ulcer, anemia, liver, heart diseases and various other disorders. In this work, thermal characteristics and metal compositions of *E. officinalis* samples were analysed and compared. This study can be used to analyse and standardize the raw plant materials available in the pharmaceutical market.

2. Materials and Methods

2.1. Collection and Authentication of Plant Materials

The fruits of *E. officinalis* were collected from the foothills of Western Ghats region of Tirunelveli District, Tamil Nadu and were authenticated by Dr. V. Chelladurai, formerly Research officer (Botany), Survey of Medicinal and Aromatic Plants Unit-Siddha, CCRAS, Palayamkottai, Tirunelveli District. The fruits were shade dried for a constant weight, powdered and named as genuine sample AMGS. Commercially available dried fruits of *E. officinalis* was procured from local market, powdered and named as market sample AMMS. Both samples were passed through sieve of size 53 μm , stored in closed vessel individually. The specimens were kept at Department of chemistry, Sri Paramakalyani College, Alwarkurichi, Tirunelveli.

2.2. Thermal Analysis

The TGA and DTA curves of the selected plant samples were recorded using NETZSCHSTA 409 PC/PG. About 50 milligram of raw dried, powdered sample was heated in alumina crucible from 35°C to 600°C at rate of 5°C per minute under Argon atmosphere. Average of three values were taken for record and the values are normalized to 100 milligram sample mass.

2.3. Morphological and Elemental Composition Analysis

2.3.1. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDAX)

Topographic, morphological images and the elemental composition of both AMGS and AMMS samples were performed using a Philips XL-20 electron microscope fitted with an energy dispersive X-ray analyzer (EDAX) that allows a qualitative detection and localization of elements in the adsorption.

2.3.2. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Exactly 1 g of ground dried plant samples was typically immersed in 10 mL of concentrated nitric acid (70%) for 12 hrs. The beaker was cooled and 2-4 mL of 60% HClO_4 was added. The samples were heated until the disappearance of the brown fumes. The contents were allowed to evaporate to a small volume and then cooled. The sample was transferred to a 50 mL flask, 5 mL of diluted (1: 1) HCl was added, and diluted to volume with distilled water [27].

The solutions were analyzed using a Perkin Elmer Model Optima 5300 DV spectrometer (Perkin Elmer, USA) ICP-OES equipped with a Ultrasonic Nebulizer CETAC U-6000AT+ (CETAC, USA) and an auto sampler AS 93-plus. Argon (purity higher than 99.995%) supplied by Linde Gas SRL (Cluj-Napoca, Romania) was used to sustain plasma and, as carrier gas. A closed-vessel microwave system Bergh of MWS-3+ with temperature control mode, (Berghof, Germany) was used for wet digestion. All Teflon digestion vessels were previously cleaned in a bath of 10% (v/v) nitric solution for 48 h to avoid cross contamination.

3. Results and Discussions

3.1. Thermal Analysis

Simultaneous TGA and DTA studies provide the torch on the physicochemical decompositions of bio components with the association of mass loss in TGA and heat changes of the reactions occur during thermal decomposition stages in DTA while heating the plant samples.

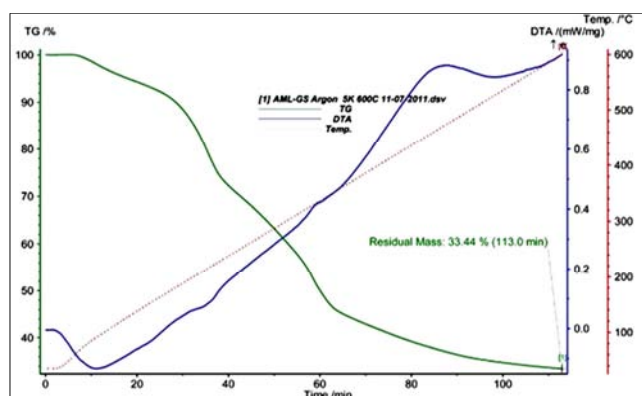
Fig. 1 shows the exemplified TGA and DTA curves of the samples AMGS and AMMS of *E. officinalis* respectively. Analytical results about the initial - end mass loss temperatures, mass loss rate on TGA curves and peak temperatures revealed on the DTA curves of both samples are shown in Table 1. Thermal decomposition curves of both samples AMGS and AMMS can be in general treated as four-stage model. TGA curves of AMGS and AMMS revealed that the first stage decomposition in the range of 58-155°C and 55-150°C, with a small mass loss 7.1% and 5.2% respectively. This is probably due to desorption of water content from plant material together with evaporation easily volatile components [28]. No significant peak on DTA curve is observed in first stage. For AMMS the second stage of decomposition in the range of 150-235°C is accompanied with strong endothermic effect on DTA curve and high mass loss of 23.8% as reflected in TGA curve whereas AMGS has shallow endothermic effect on DTA with 19.1% mass loss on TGA. Next, the third stage of decomposition is observed in the range of 230-350°C and 235-335°C with mass loss 28.4% and 21.5% for AMGS and AMMS respectively. During third stage decomposition a lower exothermic peak is occurred for the samples AMGS and AMMS. These are due to the bond breaking and burning of the low molecular components existing in the plant samples. After destruction and combustion of low molecular components of the samples,

charred residue i.e. inorganic compounds probably carbonates are decomposed in the fourth stage. The fourth stage occurs in the range of high temperature 350-600°C and 335-600°C, with 13% and 17% mass loss for AMGS and AMMS respectively. One strong exothermicity is obtained at

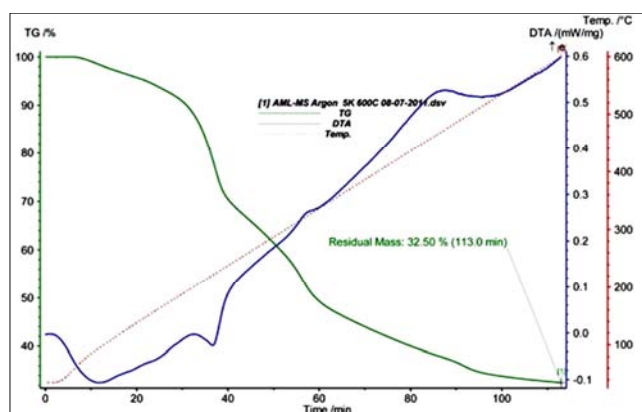
465°C for both AMGS and AMMS in this stage. Mineral residues [29] are the final products of both samples AMGS and AMMS. Residual mass values reveal that AMGS has greater content of metal composition than AMMS.

Table 1. Decomposition temperatures, Mass loss and DTA peak heights and peak temperatures of *Emblica officinalis* (L.) samples.

Decomposition Stages	TGA		DTA			
	Temp(°C)		Mass Loss (%)		Peak Temp (°C)	
	GS	MS	GS	MS	GS	MS
I	58-155	55-150	7.1	5.2	-	-
II	155-230	150-235	19.1	23.8	215	221
III	230-350	235-335	28.4	21.5	330	322
IV	350-600	335-600	13.0	17.0	465	465



(a)



(b)

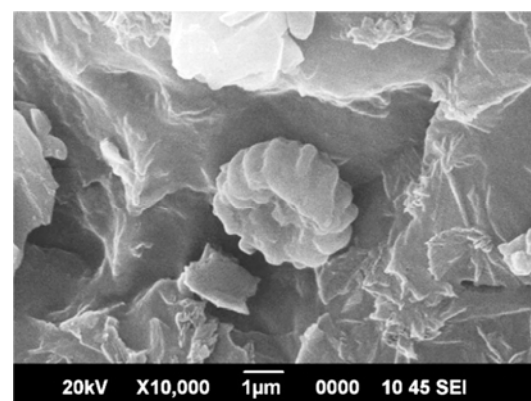
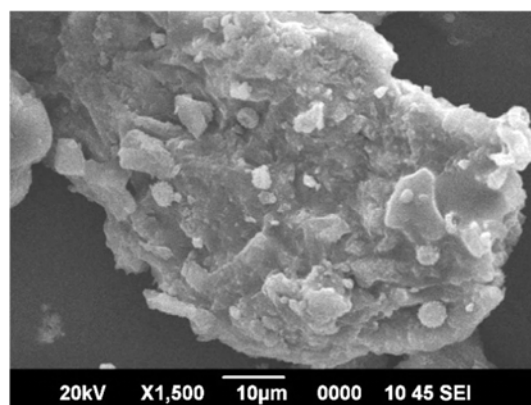
Fig. 1. TGA and DTA curve of *Emblica officinalis* samples (a) AMGS and (b) AMMS.

3.2. SEM-EDAX Elemental Analysis

SEM-EDAX, a highly qualified nondestructive technique is used to visualize the micro structures of the plant material and assess the elemental compositions on the surface of the plant sample with a minimum quantity. SEM-EDAX spectra and the elemental compositions of both AMGS and AMMS were given as Figs. 2 and 3. The SEM images of AMGS could not provide its clear morphological observation upto the equipment's maximum zoom level. However the market

sample provides clear images with wheel like granular structures. It indicates that the genuine sample composed of very fine particles which size is lesser than 1 μm and hence they are accumulated as macro particles (Fig. 2).

The EDAX results reveals that C and O were found as major constituents with almost equal amount in both AMGS and AMMS. Fair quantities of K was detected in both AMGS and AMMS as 1.81% and 0.5% by mass respectively. Notable differences were observed between the samples. Calcium responsible for bone strength and metabolism of vitamin D [30] was detected as 1.78% in only AMGS. Chlorine which helps to regulate acid alkali balance, stimulate production of hydrochloric acid, stimulate the liver to function as a filter for wastes and to distribute hormones [31] was observed as 1.16% in AMMS only.



(a)

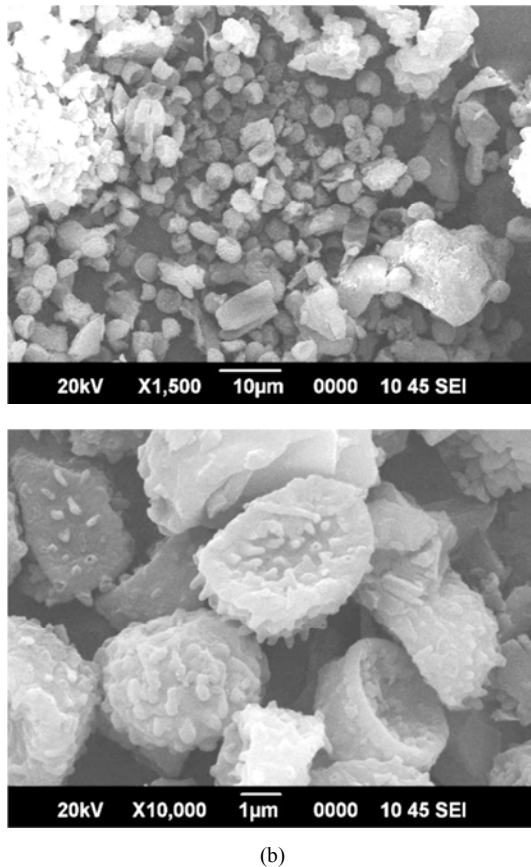
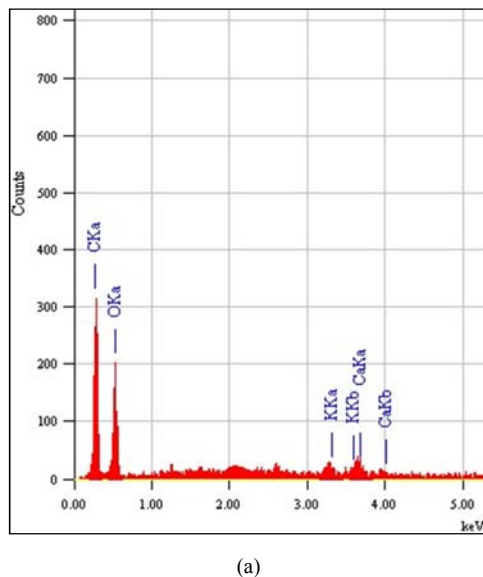
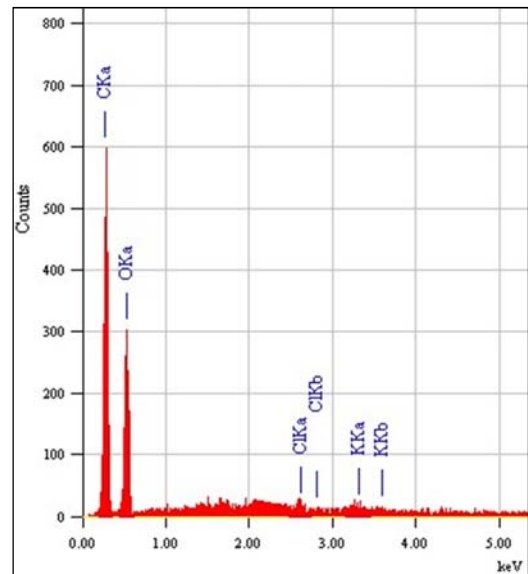


Fig. 2. SEM images of *E. officinalis* samples (a) AMGS and (b) AMMS.



(a)



(b)

Fig. 3. EDAX spectrum of *E. officinalis* samples (a) AMGS and (b) AMMS.

3.3. ICP-OES Metal Compositions

Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a convenient technique to check the availability of essential trace elements in medicinal herbs. Trace elemental analysis (Li, Ba, Ca, Mg, Bi, Cd, Al, Se, Na, K, Fe, Cr, Mn, Cu, Co, Ni, Pb and Zn) in genuine and market samples of *E. officinalis* were determined by using ICP-OES and the results are given in Table 2.

Nutrients responsible for plant growth Na, K, Ca, Mg, Fe, Ba, Bi, and Al were detected and their concentration were found to be present within the limits recommended by WHO [32] in both AMGS and AMMS samples. The results shown that minor differences were observed for the concentration of Mg, Ba and Cr and small traces of Fe, Al and Bi were observed in both samples AMGS and AMMS. Potassium together with sodium helps to regulate the water balance within the body [33]. It is observed that AMGS shows maximum concentration of potassium as 9.65 ppm and minimum concentration of sodium as 0.01ppm whereas AMMS has potassium as 8.77ppm and sodium as 0.61ppm. AMMS has greater concentration of calcium needed for strong bones, teeth, maintaining proper blood pressure and blood clotting [34]. Other metals Li, Cd, Se, Mn, Cu, Co, Ni, Pb and Zn have not been observed in both samples AMGS and AMMS.

Table 2. Elemental Compositions (ppm) of genuine and market samples of *E. officinalis*.

Element	K	Ca	Mg	Na	Fe	Mn	Cr	Li	Zn
AMGS	9.65	1.25	0.47	0.01	0.012	ND	0.109	ND	ND
AMMS	8.77	1.04	0.45	0.61	0.016	ND	0.113	ND	ND
Element	Ba	Bi	Cd	Al	Se	Cu	Co	Ni	Pb
AMGS	0.103	0.006	ND	0.023	ND	ND	ND	ND	ND
AMMS	0.099	0.014	ND	0.029	ND	ND	ND	ND	ND

ND – Not Detectable.

Collectively the both samples AMGS and AMMS have shown four decomposition stages with different mass loss rate and mineral residue percentage in TGA and an endothermic at second stage, a lower exothermicity at third stage and also a strong exothermicity at fourth stage in DTA. These observation of maximum residual mass (33.44%) of genuine sample indicate that AMGS has higher content of inorganic mineral composition than AMMS with residual mass of 32.50%. In EDAX analysis, besides carbon and oxygen as the major components of the selected samples, AMGS has potassium and calcium in detectable amount whereas AMMS has potassium and chlorine. However, ICP-OES results reveal the presence of Mg, Na, Fe, Cr, Ba, Bi and Al along with K and Ca in both samples. Except Na and Bi, all other elements in AMGS are in higher concentration than AMMS. As supported by EDAX analysis, ICP-OES also reporting that the potassium content in the AMGS sample (9.65 ppm) is higher than the market sample (8.77 ppm) of *E. officinalis*. Also the higher content of these nutritional elements in genuine sample authentically supported by the TGA analysis too as ~1% higher residual mass in GS.

4. Conclusion

The present study have been employed for the thermal pattern and determining the micro elements composition of the genuine sample of *E. officinalis* and its commercial market sample. TGA curves having residual mass variation show the thermal profiles of the selected plant samples AMGS and AMMS with mass loss of phytochemicals present in it and also genuine sample AMGS has greater concentration of inorganic mineral residues than market sample AMMS. SEM results indicate that market sample AMMS has distinct variations in the surface morphology than genuine sample AMGS. The results of EDAX and ICP-OES indicate that the concentration of macro elements K, Na, Ca, and Mg, micro elements Zn, Cu, Cr, Fe and trace elements Ba, Bi and Al in both samples AMGS and AMMS, and varied significantly in their concentration. This work shows that it is important to monitor the concentrations of metals in medicinal plant products, especially when used in the manufacture of dietary supplements or pharmaceutical products. The variations in these findings might cause by the ecological and geographical conditions, soil compositions, cultivation, processing and storage of plant samples. However, the current study gives a new trustworthy method to standardize the trade potential medicinal herb of *Emblca officinalis* for its authenticity, safety and efficacy.

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