

Ash properties of some dominant Greek forest species

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Abstract

The elemental and chemical wood ash compositions of six dominant Greek fuels was investigated using a variety of techniques, including thermal gravimetric analysis (TG), differential thermal analysis (DTA), atomic absorption spectroscopy (AAS) and X-ray diffraction (XRD). In addition, the alkalinity of wood ash was determined by titration. The ash was prepared by combustion at low (600 °C), middle (800 °C) and high temperatures (1000 °C). The ash composition is very important because thousands of hectares of wildlands are burned annually in Greece. The resulting deposits affect soil properties (i.e., pH) and provide a source of inorganic constituents (i.e., Ca, K, Na, Mg, etc.), while the most soluble compounds (i.e., sodium and potassium hydroxides and carbonates) do not persist through the wet season. The samples selected were: *Pinus halepensis* (Aleppo pine), *Pinus brutia* (Calabrian pine), *Olea europaea* (Olive), *Cupressus sempervirens* (Italian cypress), *Pistacia lentiscus* (Mastic tree), *Quercus coccifera* (Holly oak).

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1. Introduction

Wild fires burn thousands of hectares all over the world each year. The produced white ash, termed as “wood ash”, comprises the inorganic constituents of wood that remain after burning. The wood ash is a highly alkaline matter (pH 9–13.5) and its disposal is a growing problem as environmental regulations become more stringent [1]. Wood ash has been used in agriculture as soil amendment because it is an excellent source of potash (potassium), lime and other plants nutrients [1–6]. It has also been used as binding agent, glazing agent in the ceramic industry, road base, additive in cement industry, and alkaline material for the neutralization of wastes [1,7].

Etiegni and Campbell [2] have found that the ash yield and its chemical composition change with combustion temperature, i.e. the yield decreases approximately 45% as the combustion temperature increases from 538 to 1093 °C. The major elements which were determined by atomic absorption

and atomic emission spectrometer (AAS/AES), with the respective concentration values at combustion temperatures of 538 and 1093 °C, were: calcium (187 and 265 mg/g), potassium (110 and 4 mg/g), magnesium (60 and 89 mg/g), silicon (34 and 35 mg/g), manganese (60 and 89 mg/g), aluminum (10 and 11 mg/g), phosphorous (17 and 25 mg/g), iron (9 and 17 mg/g), sodium (3 and 0.1 mg/g), zinc (3 and 0.05 mg/g). Based on the above measurements, Etiegni and Campbell [2] concluded that potassium, sodium, zinc and carbonate content decreased with increasing temperature, whereas other elements remained almost constant (i.e., silicon, aluminum) or increased (i.e., calcium, magnesium, manganese, iron, chromium, lead, phosphorous). They have also suggested, based on X-ray diffraction (XRD) measurements that calcium silicate may be responsible for some of the swelling that occurs when ash and water react. Scanning electron microscope (SEM) analysis in their study indicated that ash had an average particle size of 230 μm and contained large porous carbon particles and many irregularly shaped inorganic particles.

Misra et al. [8] have investigated the elemental and chemical composition of ash of various wood species as a function

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of combustion temperature, using thermal gravimetric analysis (TG), differential thermal analysis (DTA), inductively coupled plasma emission spectroscopy (ICP-ES), and X-ray diffraction. Their study showed that at low temperatures (600 °C) the ash contained mainly CaCO₃ and K₂Ca(CO₃)₂, whereas at high temperature (1300 °C) CaO and MgO were the main compounds. Erich and Ohno [9] have applied a procedure suggested by the Association of Official Analytical Chemists (AOAC) for the titrimetric determination of calcium carbonate equivalence of wood ash.

However, the data published on the composition of forest species ashes were not as detailed as for the ashes of coal. According to several authors [10,11], the composition of forest ash depends on various factors, including, type of forest species, part of plant combusted (bark, wood, leaves), plant age, type of soil, climate, conditions of combustion, etc. As a consequence, the available data on the properties of wood ash are very variable and generalizations are therefore difficult to make.

In this paper, the elemental and molecular composition of the wood ash of six dominant Greek forest fuels was investigated using thermal gravimetric analysis, differential thermal analysis, atomic absorption spectroscopy, X-ray diffraction and titrimetry. The objectives of this research were to determine the yield, chemical composition and mineralogy of wood ash produced by intense burning during forest fires and to evaluate its effects on soil properties, on the availability of nutrient elements, as well as its impact on the environment.

2. Experimental

2.1. Thermal analysis

Thermogravimetric (TG) and differential thermal analysis were carried out using a Mettler TGA/SDTA 851 module supported with a PC and software for control and data handling. The forest species ash samples, approximately 20 mg in weight, were introduced into an open 0.07 ml platinum sample pan and heated first from 25 to 600 °C with a linear heating rate of 50 °C min⁻¹ and then up to 1300 °C with a linear heating rate of 25 °C min⁻¹. All runs were carried out in nitrogen atmosphere at a flow rate of 50 ml min⁻¹. Heat-up temperatures were limited to a maximum of 1300 °C as the TG instructions order. The chosen heating rate conditions are close to the real fire spread conditions developed in forest fires [25] and match those reported by other researchers [8].

2.2. Elemental analysis

Elemental analysis was carried out using a Perkin-Elmer, model 330, atomic absorption spectrometer. Samples for AAS were prepared by dissolving approximately 50 mg of the dried ash in 10 ml concentrated hydrochloric acid 20% (w/w). The solution was then heated, filtered and the precipitate was washed with deionized water. The filtrate was diluted

to 100 ml and analyzed by AAS. Specifically, the determination of Cl⁻ was carried out by a Pionex ion chromatograph, model GS50, after dissolving the ash samples with nitric acid 5% (w/w).

2.3. Titrimetry

2.3.1. Titration for measuring the alkalinity of ash leachate

The forest species ash (0.5 g) was mixed with 50 ml of distilled water and agitated for 48 h. The mixture was centrifuged, filtered through a 0.2 μm membrane filter, and then titrated with 0.5 M HCl using an Orion, model 950 Ross FASTQC, automatic potentiometric titrator. The sensor was a pH electrode, type Orion-72 BN. Based on the titration curves (pH versus V) the soluble alkalinity, mainly due to the hydroxide and carbonate content, was determined [2,12].

2.3.2. Titration for measuring the total alkalinity of ash

A second titration experiment was carried out measuring the total alkalinity of wood ash. The wood ash (0.05 g) was diluted with 10 ml of 1 M HCl under heating. The residual acid was back titrated with 1 M NaOH using the automatic potentiometric titrator, mentioned earlier. Based on the titration curves (pH versus V) the total alkalinity, mainly due to the carbonate and hydroxide content, was determined.

2.4. X-ray diffraction analysis

The samples were analyzed in a Siemens D5000 X-Ray Diffractometer using a copper target to generate the X-rays (wavelength = 1.5405×10^{-10} m). The wood ash samples for XRD were first finely ground and then mounted on a sample holder. The powder was ground fine to ensure random orientation of the crystals so that there are sufficient amount of crystals to generate detectable signals of all angles and that the background noise is kept to a minimum.

2.5. Samples

Tests were conducted on six forest fuels: *Pinus halepensis*, *Pinus brutia*, *Olea europaea*, *Cupressus sempervirens*, *Pistacia lentiscus*, *Quercus coccifera*. The selected species are very common in the Mediterranean region and often devastated by forest fires.

The sample collection site of all forest species was the mountainside Kalopoula of Imittos, near Athens, located W–NW with dominated rock limestone, geographic coordinates 37°58'13"N and 23°48'20"E, height 487 m and average slope 70%. The date of collection was 26 August 2004. All samples were mature foliage, collected after a long drought period in order to avoid moisture effects. Four individual plant species were collected from the field and immediately brought intact to the laboratory. The samples were washed with deionized water and then dried at 60 °C in a vacuum of

100 mmHg until constant weight within 1 mg. The approximate drying period was 48 h.

The forest species samples were dry ashed at 600, 800 and 1000 °C according to standard methods [13,14].

3. Results and discussion

3.1. Thermal analysis

The TG and DTG graphs of forest species ashes prepared at 600 °C are presented in Fig. 1 under certain operating conditions. To note that variables such as sample mass, heating

rate and gas flow have a marked effect on the profile of TG and DTG curves [15,16].

The mass loss observed in the temperature range 350–650 °C (Fig. 1a) is mainly attributed to the decomposition of MgCO_3 , $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$, according to the following equations with the respective TG peak temperatures (T_p) given in the literature [17–20]:

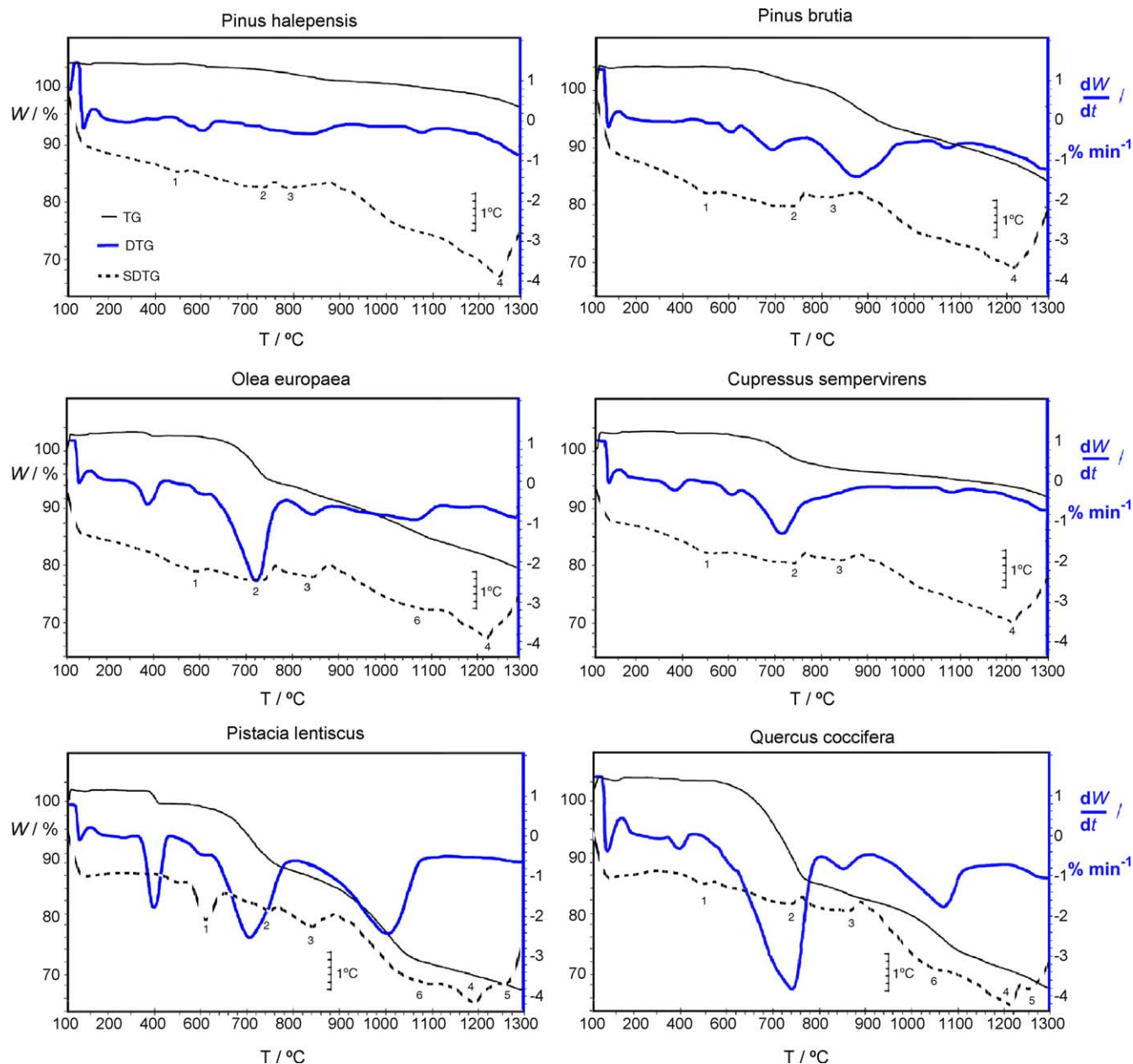
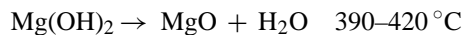
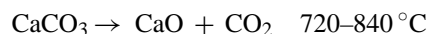


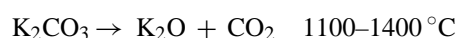
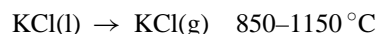
Fig. 1. TG, DTG and SDTA curves of forest species ashes prepared at 600 °C.

The above hydroxides were formed, after the thermal treatment of wood species, by reacting the respective oxides with the ambient moisture.

The mass loss observed in the temperature of 650–900 °C (Fig. 1) is predominantly due to the decomposition of CaCO_3 , according to the equation and the respective TG peak temperature (T_p) given in the literature [15,18,19,21,22]:



Finally, the masses loss recorded between 900 and 1300 °C (Fig. 1) are mainly due to the vaporization of KCl and the decomposition of K_2CO_3 , according to the equations with the respective TG temperature ranges (T_i – T_f) reported in literature [23]:



Dissociation of sulfates (i.e., CaSO_4 and K_2SO_4) also takes place at temperatures above 1000 °C [23].

Similar results were obtained by TG/DTG analysis of forest species ashes prepared at 800 and 1000 °C.

Based on the TG diagrams, the mass losses at the temperature ranges: 350–650, 650–900, 900–1300 °C, and the mass residue at 1300 °C were determined (Table 1). The data

reported are the average of three replicate measurements with relative standard deviations below 10% and detection limit 1.0%. The unexpected high mass loss recorded in some ash samples with high content in calcium (i.e., *P. lentiscus* at 800 and 1000 °C) is due to the decomposition of Ca(OH)_2 and CaCO_3 . These compounds were formed, after the ashing procedure via the reaction of CaO with the ambient moisture and CO_2 . The results given in Table 1 are consistent with those of other researchers [8].

The mass losses observed at temperatures between 350 and 1300 °C due to the decomposition of hydroxides (both calcium and magnesium) and carbonates (calcium, magnesium and potassium) were confirmed by the simultaneous thermal analysis (SDTA) results shown in Fig. 1. The SDTA curves have similar shapes for all ash samples examined. Five distinct endothermic peaks are observed in the SDTA graphs (Fig. 1). The first peak (No. 1) in the temperature region 350–450 °C corresponds to the decomposition of hydroxides (both calcium and magnesium), the second (No. 2) 500–600 °C to the decomposition of MgCO_3 , the third (No. 3) at 660–750 °C to the decomposition of CaCO_3 and the fourth and fifth (No. 4, No. 5) at 1100–1300 °C are attributed to the decomposition of K_2CO_3 . Finally, the wide peak (No. 6) appeared in the temperature region 900–1050 °C of some forest species is attributed to the vaporization of KCl .

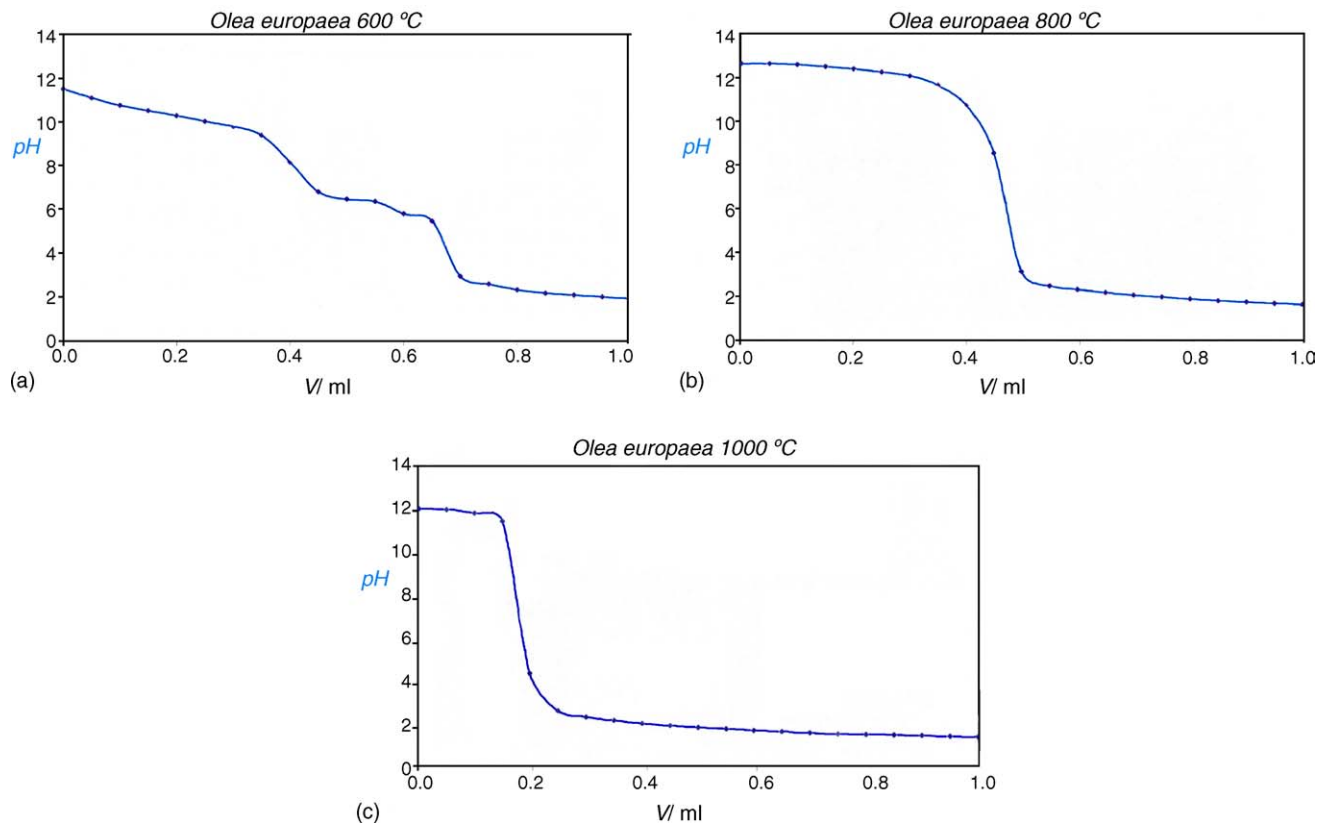


Fig. 2. Titration curves of *Olea europaea* ash leachate with 0.5 M HCl. Ash prepared at: (a) low temperature (600 °C), (b) moderate temperature (800 °C) and (c) high temperature (1000 °C).

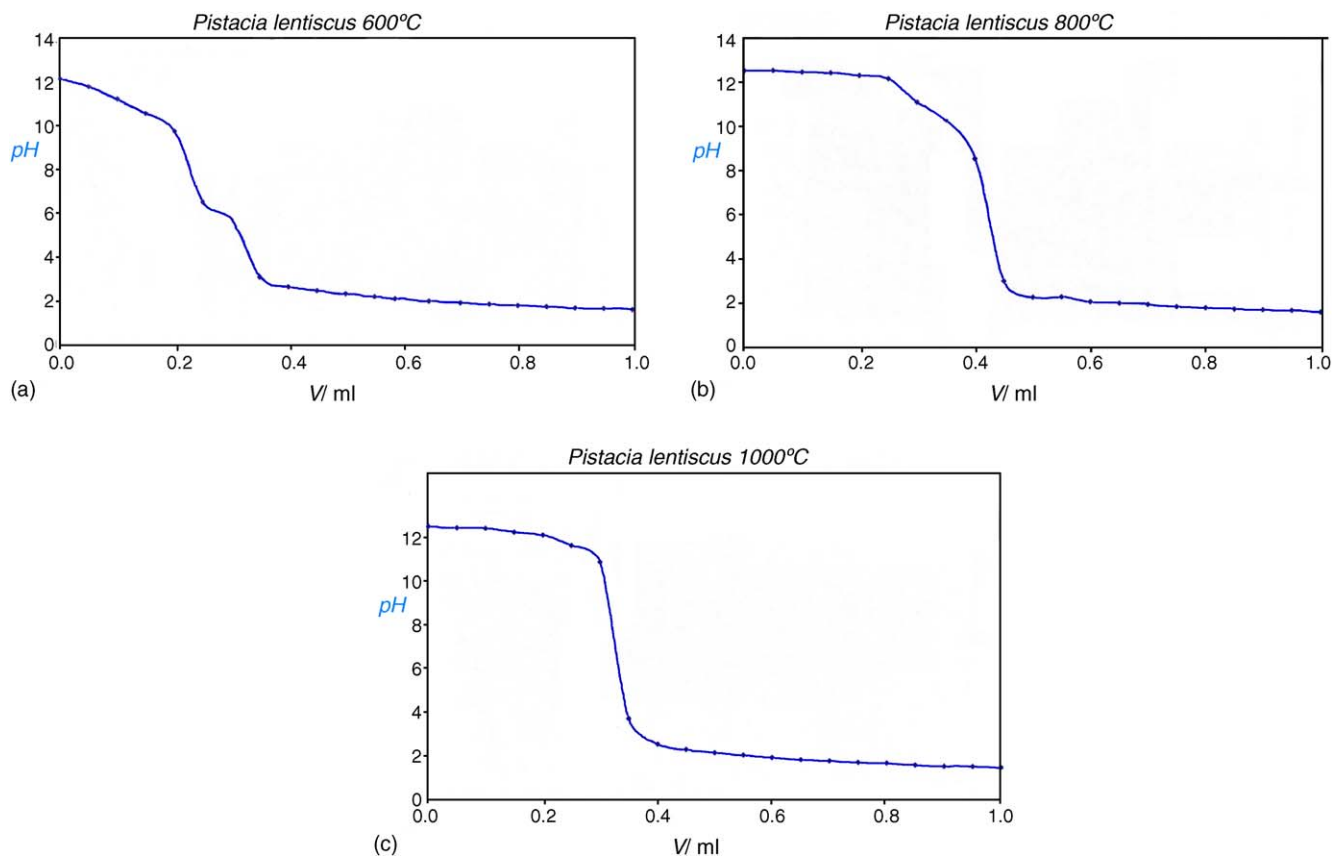


Fig. 3. Titration curves of *Pistacia lentiscus* ash leachate with 0.5 M HCl. Ash prepared at: (a) low temperature (600 °C), (b) moderate temperature (800 °C) and (c) high temperature (1000 °C).

Table 1
TG analysis data of various forest species ashes as a function of combustion temperature

Forest species	Ash prepared at (°C)	Mass loss (%)			Mass residue (%) 1300 °C
		350–650 °C	650–900 °C	900–1300 °C	
<i>Pinus halepensis</i>	600	<1.0	2.3	5.0	92.1
	800	<1.0	<1.0	2.2	97.9
	1000	<1.0	<1.0	1.8	97.5
<i>Pinus brutia</i>	600	<1.0	7.8	12.0	79.6
	800	<1.0	<1.0	2.7	97.7
	1000	<1.0	<1.0	1.6	96.6
<i>Olea europaea</i>	600	1.5	10.7	12.2	75.8
	800	<1.0	<1.0	2.1	97.4
	1000	<1.0	<1.0	1.2	99.2
<i>Cupressus sempervirens</i>	600	1.1	5.9	4.6	88.5
	800	1.9	<1.0	2.7	95.3
	1000	<1.0	<1.0	1.5	98.3
<i>Pistacia lentiscus</i>	600	6.1	10.0	13.5	65.5
	800	6.0	<1.0	2.5	93.0
	1000	4.8	<1.0	2.1	91.3
<i>Quercus coccifera</i>	600	3.1	18.4	15.6	63.6
	800	<1.0	<1.0	4.4	94.8
	1000	<1.0	<1.0	2.2	97.7

3.2. Elemental analysis

Table 2 lists the concentrations of the major metal elements (K, Na, Ca, Mg, Mn, Fe, Zn) and their variations with temperature, for all forest species ashes examined, determined by AAS. In the same table the ash content (% w/w) of forest species is shown. The measurements reported in Table 2 are the average values of four replicate analysis tests, while the relative standard deviations determined were below 10%.

P. lentiscus ash at 1000 °C has the highest amount of calcium (52.7%) and *P. brutia* ash at 600 °C has the highest amount of potassium (21.8%), compared to all other ash types. Sodium is generally low in all ash samples examined, i.e. 2.43% (w/w) for *P. brutia* at 800 °C.

The calcium and magnesium content of ashes increased with increasing temperature (Table 2) due to the thermal decomposition of $MgCO_3$, $CaCO_3$, K_2CO_3 , and the simultaneous volatilization of potassium oxide formed after decom-

position. The latter also leads to a decrease in potassium concentration of the ash with increasing temperature (Table 2). The sodium content was first increased in the temperature range 600–800 °C and then decreased from 800 to 1000 °C, except *P. lentiscus* ash samples. Finally, manganese, iron and zinc are present in relatively small amounts. Mn and Fe content increased, while Zn decreased with increasing temperature (Table 2).

The above results are in agreement with other works [2,8] as well as with TG analysis data reported in Table 1.

3.3. Titrimetry

3.3.1. Titration for measuring the alkalinity of ash leachate

The titration of ash leachates with 0.5 M HCl yielded to three different equivalence points, as is shown in Figs. 2 and 3, for *O. europaea* and *P. lentiscus*. Similar results were also obtained for all the other forest species examined.

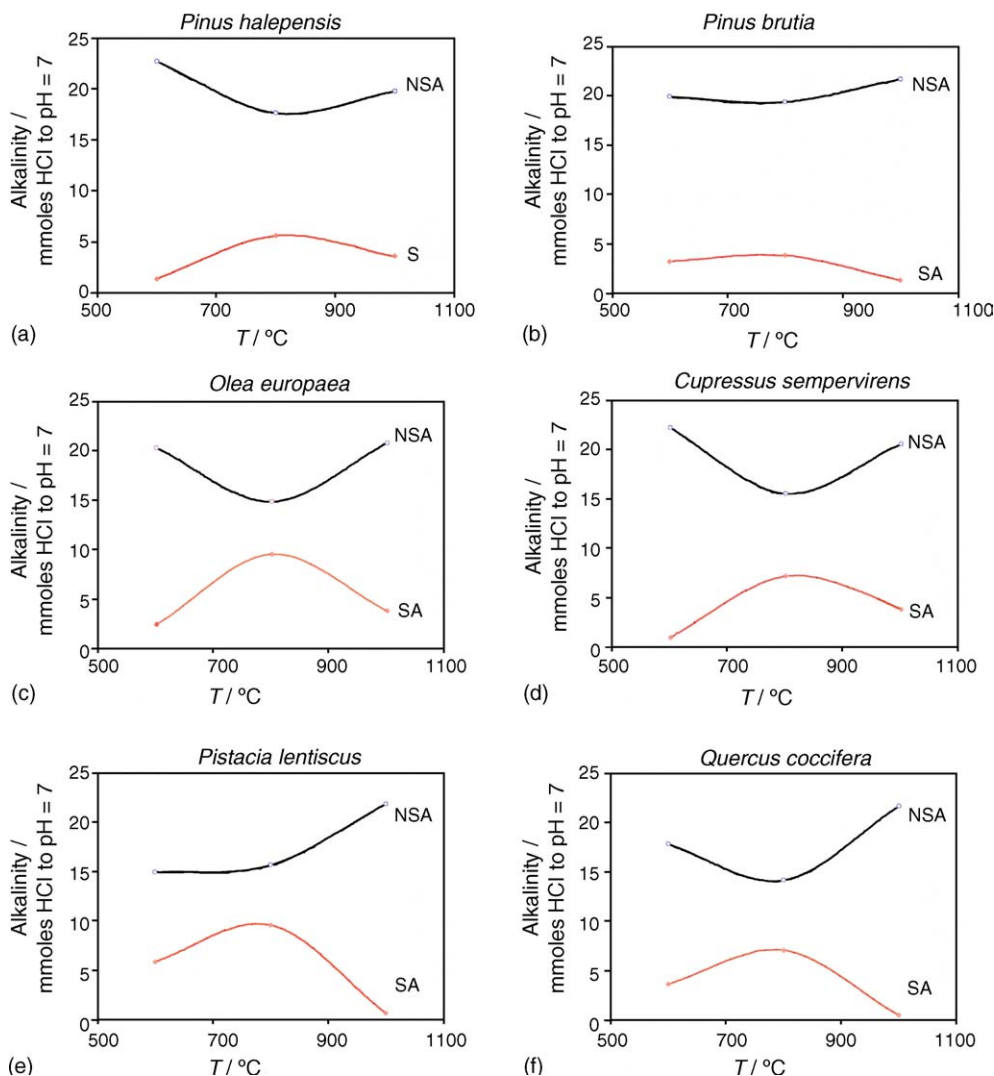


Fig. 4. Alkalinity vs. temperature of ash preparation. NSA: non-soluble alkalinity; SA: soluble alkalinity.

Table 2
Elemental and titrimetric analysis data of various forest species ashes as a function of combustion temperature

Forest species	Ash (°C)	Ash content (% w/w)	K (% w/w)	Na (% w/w)	Ca (% w/w)	Mg (% w/w)	Mn (% w/w)	Fe (% w/w)	Zn (% w/w)	Si (% w/w)	Ti (% w/w)	Cl (% w/w)	P (% w/w)	S (% w/w)	S.A. (mmol HCl/g ash)	T.A. (mmol HCl/g ash)	N.S.A. (mmol HCl/g ash)
<i>Pinus halepensis</i>	600	3.27	13.00	1.78	19.2	8.84	1.12	0.91	0.28	2.55	0.09	2.17	3.13	3.61	1.35	24.06	22.71
	800	2.97	6.78	2.18	22.3	8.81	1.20	0.85	0.02	2.59	0.09	n.d.	3.17	3.69	5.60	23.24	17.64
	1000	2.93	1.40	0.49	25.4	9.75	1.37	1.25	0.01	2.68	0.09	n.d.	3.30	3.81	3.63	23.44	19.81
<i>Pinus brutia</i>	600	2.39	18.30	1.23	16.9	9.59	1.69	0.80	0.24	1.49	0.08	1.43	1.62	2.36	3.07	22.84	19.77
	800	2.03	8.29	2.43	22.6	13.1	1.75	0.86	0.02	1.55	0.08	n.d.	1.67	2.45	3.70	22.94	19.24
	1000	2.01	1.28	0.52	29.6	14.1	1.91	1.88	0.01	1.73	0.09	n.d.	1.87	2.62	1.22	22.78	21.56
<i>Olea europaea</i>	600	4.94	13.01	0.52	32.8	4.22	1.15	1.67	0.50	0.55	0.15	0.85	1.56	2.89	3.34	31.68	28.34
	800	4.13	7.05	0.92	42.8	5.81	1.23	1.54	0.04	0.58	0.16	n.d.	1.64	3.04	13.26	34.00	20.74
	1000	4.05	0.61	0.17	46.4	6.26	2.07	2.15	0.01	0.67	0.18	n.d.	1.86	3.44	5.32	34.42	29.10
<i>Cupressus sempervirens</i>	600	3.86	7.74	0.87	22.2	6.24	0.74	1.05	0.32	1.29	0.07	2.99	2.08	2.90	1.05	31.84	30.79
	800	3.43	4.61	1.02	28.9	7.93	1.14	1.62	0.03	1.33	0.10	n.d.	2.14	2.99	9.75	31.20	21.45
	1000	3.05	0.47	0.15	35.8	9.12	1.81	1.95	0.01	1.40	0.11	n.d.	2.26	3.15	5.56	34.08	28.52
<i>Pistacia lentiscus</i>	600	3.76	13.3	2.29	26.1	6.40	1.46	1.24	0.38	0.57	0.12	1.37	2.39	3.03	6.87	24.66	17.79
	800	2.70	5.31	1.90	45.9	8.57	2.03	1.54	0.04	0.60	0.13	n.d.	2.51	3.14	11.34	30.00	18.66
	1000	2.69	1.46	0.22	52.7	11.2	2.29	2.02	0.01	0.65	0.14	n.d.	2.87	3.60	0.70	26.78	26.08
<i>Quercus coccifera</i>	600	3.79	10.71	0.51	25.9	7.79	1.45	1.23	0.37	1.13	0.11	0.43	1.73	2.62	5.71	34.12	28.41
	800	2.78	4.64	0.96	37.1	10.2	2.04	1.41	0.03	1.24	0.12	n.d.	1.91	2.87	11.19	33.76	22.57
	1000	2.70	1.23	0.12	38.8	14.1	2.33	2.05	0.01	1.51	0.14	n.d.	2.30	3.49	0.74	35.34	34.60

S.A.: soluble alkalinity-neutralisation to pH 7; T.A.: total alkalinity-neutralisation to pH 7; N.S.A.: non-soluble alkalinity-neutralisation to pH 7; n.d.: not determined.

Table 3
Crystalline compounds in forest species ashes identified by X-ray diffraction analysis

Forest species	Ash prepared at (°C)	Compounds in ashes ^a
<i>Pinus halepensis</i>	600	CaO, MgO, K₂CO₃·CaCO₃ (fairchildite), (CaMg)CO ₃ , K ₂ SO ₄ , K ₂ CO ₃
	800	CaO, MgO , K ₂ SO ₄ , K ₂ CO ₃
	1000	CaO, MgO , K ₂ SO ₄ , K ₂ CO ₃
<i>Pinus brutia</i>	600	CaCO₃, MgO , K ₂ CO ₃ ·CaCO ₃ (fairchildite)
	800	CaO, MgO , K ₂ CO ₃
	1000	CaO, MgO , K ₂ CO ₃ , K ₂ Si ₄ O ₉
<i>Olea europaea</i>	600	CaO, KCl, K₂CO₃·CaCO₃ (fairchildite), K ₂ CO ₃ , MgO, SiO ₂ , K ₂ SO ₄
	800	CaO, MgO , K ₂ SO ₄
	1000	CaO, MgO , K ₂ SO ₄
<i>Cupressus sempervirens</i>	600	CaO, MgO, Ca(OH)₂, K₂CO₃, K₂Ca₂(SO₄)₃ , KCl, K ₂ SO ₄
	800	CaO, MgO, K₂CO₃ , Ca(OH) ₂ , K ₂ Ca(CO ₃) ₂ , K ₂ SO ₄
	1000	CaO, MgO, K₂CO₃
<i>Pistacia lentiscus</i>	600	KCl, Ca(OH)₂, MgO, (CaMg)CO₃ , K ₂ Ca(CO ₃) ₂ , K ₂ CO ₃ , CaO
	800	CaO, MgO , K ₂ CO ₃ , Ca(OH) ₂
	1000	CaO, MgO, K₂CO₃
<i>Quercus coccifera</i>	600	(CaMg)CO₃, MgO, K₂CO₃·CaCO₃ (fairchildite), K ₂ CO ₃
	800	CaO, MgO , K ₂ CO ₃
	1000	CaO, MgO , K ₂ CO ₃

^a Compounds in bold are the main constituents of the corresponding ash.

The equivalence point at pH 7 is mainly attributed to hydroxides neutralization. The equivalence point at approximately pH 8.3 corresponds to half-neutralization of carbonates, according to the equation: $\text{CO}_3^{2-} + \text{H}_3\text{O}^+ \rightarrow \text{HCO}_3^- + \text{H}_2\text{O}$, while at pH around 4 the neutralization of carbonates is completed: $\text{CO}_3^{2-} + 2\text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{CO}_3 + 2\text{H}_2\text{O}$ [24]. Based on the above titration curves, the concentration values of hydroxides and soluble carbonates of all ashes examined can be determined [12].

The soluble alkalinity was determined by measuring the number of mmol of HCl required to neutralize 1 g of ash leachate to pH 7 and the results are presented in Table 2.

The data reported in Table 2 are the average values of three replicate titration analysis tests, and the relative standard deviations determined were below 5%.

O. europaea ash at 800 °C has the highest value of soluble alkalinity (13.26 mmol HCl to pH 7) and *P. lentiscus* ash at 1000 °C has the lowest one (0.70 mmol HCl to pH 7).

The decreasing of carbonate content of ashes with increasing temperature (Figs. 2 and 3) is mainly due to the thermal decomposition of MgCO₃, CaCO₃ and K₂CO₃. The latter also leads to increase in hydroxide concentration of the ash with temperature up to 800 °C. However, in the temperature range 800–1000 °C, the decreased concentration of OH⁻ with increasing temperature is due to the volatilization of potassium oxide (Figs. 2b, c, 3b and c). These results are in agreement with other works [2].

3.3.2. Titration for measuring the total alkalinity of ash

The total alkalinity was determined by back-titrating the ash samples after treatment with hydrochloric acid 1 M, using as standard solution NaOH 1 M. The total alkalinity was expressed in mmol HCl for neutralizing 1 g ash to pH 7

(Table 2). The total alkalinity is mainly due to the carbonates content for low temperature ashes (600 °C) and to the metallic oxides content (i.e. CaO, MgO, K₂O) for moderate (800 °C) and high temperature (1000 °C) ashes, respectively. *Q. coccifera* ash at 1000 °C has the highest value of total alkalinity (35.34 mmol HCl to pH 7) and *P. brutia* ash at 600 °C has the lowest one (22.84 mmol HCl to pH 7).

The non-soluble carbonate content was calculated by subtracting the soluble alkalinity from the total one (Table 2).

The ash temperature preparation affects its alkalinity properties (Fig. 4). The soluble alkalinity increases from 600 to 800 °C, and decreases from 800 to 1000 °C, while the insoluble alkalinity decreases from 600 to 800 °C and then increases from 800 to 1000 °C.

3.4. X-ray diffraction analysis

The crystalline compounds in ashes, identified by XRD diffraction, are displayed in Table 3. Fig. 5 presents the XRD patterns in the case of *O. europaea*.

The main conclusions drawn from the XRD patterns are the following.

The main type of compounds identified in the forest species ashes examined were oxides, carbonates and sulfates of Ca, Mg and K. Ashing at high temperature ($T > 600$ °C) promotes the decomposition of carbonates, i.e. (CaMg)CO₃ (dolomite), K₂CO₃·CaCO₃ (fairchildite), the sublimation of chlorides, i.e. KCl and in some cases the formation of alkali/alkali earth silicates (Ca–Si–O or K–Si–O). The only salts present at higher temperature were K₂SO₄ and K₂CO₃.

The crystalline compounds were found to contain mainly Ca, Mg and in a lesser extend K in all ashes studied. Calcium and magnesium were mainly in form of oxides, while

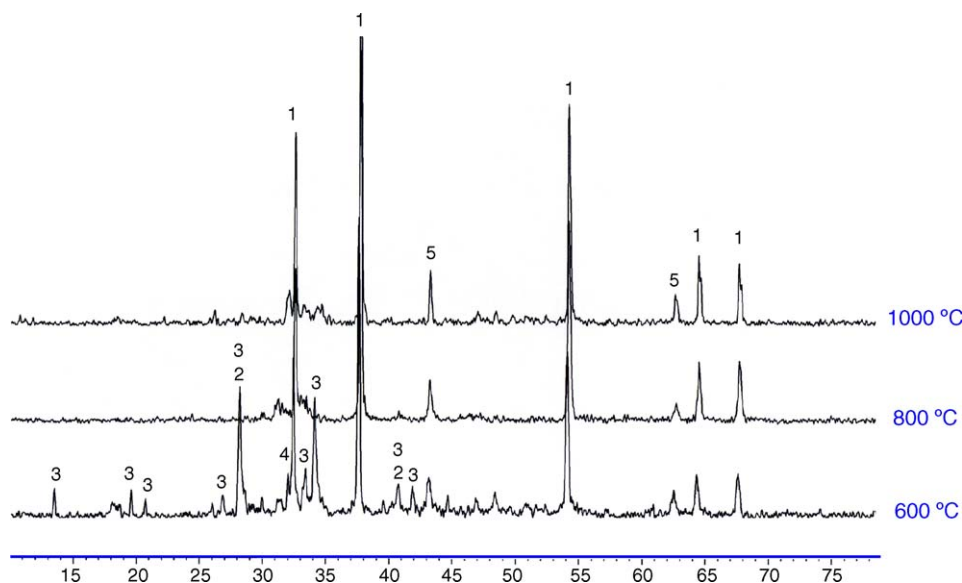


Fig. 5. X-ray diffraction patterns of *Olea europaea* ashes prepared at low temperature (600 °C), moderate temperature (800 °C) and high temperature (1000 °C): (1) CaO; (2) KCl; (3) $K_2CO_3 \cdot CaCO_3$; (4) K_2CO_3 ; (5) MgO.

potassium as potassium carbonate or calcium–potassium carbonate (fairchildite). In the case of *O. europaea* and *P. lentiscus* the main potassium compound was KCl. The above results were confirmed by AAS and TG analysis (Tables 1 and 2).

MgO and CaO detected in wood ashes prepared at 600 °C were probably formed via combustion of magnesia and calcium organic matter rather than via decomposition of $MgCO_3$ and $CaCO_3$, which takes place at higher temperatures. In some cases, $Ca(OH)_2$ (portlandite) was detected in the sintered products. This compound is formed after the thermal treatment through the reaction between CaO and ambient moisture.

4. Conclusions

The chemical composition of wood ash prepared from various forest species has been determined by combining simultaneous thermal analysis with titrimetric and spectrometric analytical techniques. The ash temperature preparation affects significantly its chemical composition. The metal content (i.e., Ca, Mg, K) tended to increase and carbonate and hydroxyl to decrease with increasing ash preparation temperature. The soluble alkalinity first increased within the temperature (600–800 °C) and then decreased (800–1000 °C).

The preparation of the ashes took place in a laboratory furnace and lasted several hours, therefore, the ash properties determined are representative of a rather equilibrium situation than an in situ forest fire. However, the temperature range chosen for the preparation of ashes (600–1000 °C) is very commonly developed in wildland fires [25]. Thus, the reported data can be used in order to correlate the ash com-

position with the temperature developed and the rate of fire spread in real forest fires.

The chemical properties determined are important criteria in recycling and disposing of wood ash. Also, the presence of KCl in wood ashes has been reported as one of the main drawbacks of using biomass in boilers, causing increased slagging, fouling and corrosion in boilers [23]. In addition, the ignition properties of forest species reported in previous works [26–31] may be interpreted by their ash composition. For example, the presence of calcium magnesium carbonates in the forest species mass residue, such as huntite $Mg_3Ca(CO_3)_4$, acts as a fire retardant matter [32].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tca.2005.06.041](https://doi.org/10.1016/j.tca.2005.06.041).

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