

The total ash content in young Albanian oak trees (*Quercus cerris*.L and *Quercus frainetto* Ten)

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Abstract:

Turkey oak (Quercus cerris L.) and Italian oak (Quercus frainetto Ten) are two wood species widely distributed in Albania, but less investigated for the chemical composition and in particular for their ash content. The aim of this work is to investigate the content of the total inorganic components in the stem wood of those species from different regions. From this study was found that the ash content varies between two different species of trees, grown in the same region and also this variability exists within the same tree species, but grown in different regions. In Quercus frainetto Ten the content of ash's range varies from 0.51% (Ulëz) to 1.19% (Dibër), while in Quercus cerris L. the content of ash's range varies from 0.54% (Ulëz) to 1.39% (Dibër). According to the statistical result was found a positive correlation ($r = 0.58$ at a $p=0.014$) between the ash content in Quercus frainetto Ten and age of the trees; and a positive correlation ($r = 0.57$ at a $p=0.021$) between the ash content in Quercus cerris.L and diameters of the woods.

Key words: Turkey oak, quercus frainetto Ten, ash, stem wood, bark, heartwood.

Introduction

The genus *Quercus* is one of the most important clades of woody angiosperms in the Central and Western Europe, in terms of

species diversity, ecological dominance, and economic value (NIXON KC 2006). The genus *Quercus* in Albania is mainly represented by Turkey oak (*Quercus cerris* L.), Italian oak (*Quercus frainetto* Ten.), pedunculate oak (*Quercus robur* L) and sessile oak (*Quercus petraea* Liebl.). *Q.cerris* and *Q.frainetto* are the most widespread species in Albania, covering 132910 ha (30.8 % of overall forest area) (ANFI 2004). In Albania, there are few studies related to this species focused on silvicultural aspects (DIDA M 2003), but less investigated for the chemical composition and in particular for their ash content.

The aim of this work is to investigate the content of the total inorganic components in the stem wood of those species from different region.

The inorganic composition of wood is usually referred to total ash content which is an approximate measure of the mineral salt and other inorganic materials in the fiber after combustion at temperature of 575 ± 25 °C. A tree takes minerals from the forest soil through its root system and transports them to the stem and crown by sap flow. The greatest concentration of minerals occurs in the parts of the tree where the life processes take place.

The composition of mineral matter in wood depends somewhat on the soil conditions under which the tree grew, and the location of the sample within the tree. A number of mineral constituents are necessary for plant growth. These and other minerals are transported from the soil through the roots. Ash from woody biomass comes from the presented minerals in the structure of trees and shrubs in addition to any soil contamination. Properties of wood ash depend on a variety of factors including type of tree or shrub, part of the tree or shrub (bark, wood, leaves), type of soil and climate and conditions of combustion (Demeyer, A 2001) .

The minerals are comprised mainly of salts of calcium, potassium and magnesium, with other salts in lesser amounts.

The acid radicals are carbonates, phosphates, silicates, sulfates and oxalates. In some species, sub micron, crystals of calcium oxalate (CaC_2O_4) have been observed (Mc. Millin1969). For bark, in addition to the minerals transported from the soil, there are windblown minerals and minerals picked up during harvesting. Relatively little mineral matter is extractable from wood with water. The ash content of wood grown in the temperate zones is 0.1-1.0%, whereas wood grown in the tropical and subtropical zones contains up to 5% ash (Fengel, D. and Wegener 1984).

The ash content of tree components varies according to site fertility, species, tree size and age, and season. Young trees tend to have higher ash content than mature-trees (Hakkila 1989). Ash content did not correlate with the rate of growth rings and basic density of wood. [9] (Mc. Millin1969) Bark is generally higher inorganics than normal wood. Bark has 10-20 times the ash content of wood (Kenneth W. 1987)

Oak forests in Albania are managed in two ways: coppice and high forests. However, there are some forests under mixed management. In general, about 74% of oak forests are coppice and 26% are high forests. Because they are managed as coppice, oak forests are often clear cut and managed with short rotation. This is the reason why they are so young. (Stafasani M 2015)

Material and Methods

The study was carried out in six sites allocated along longitudinal gradient. So in the north-east part our sampling sites were Kukesi (KU) [**Longitude** 20° 23' 35" E; **Latitude** 42° 05' 01" N and **Altitude (m. a.s.l)** 365]and Diber (DI)[**Longitude**20° 23' 46" E ; **Latitude** 41° 45' 07 " N and **Altitude (m. a.s.l)** 616]. For the northern central part of Albania we chose Ulza (UL) [**Longitude** 19° 54' 07" E ; **Latitude** 41° 39' 28 " N and **Altitude (m. a.s.l)** 241] and Rresheni (RR)[**Longitude** 19° 53' 10" E; **Latitude** 41° 48' 09

" N **Altitude (m. a.s.l)** 240]sites, while from southern-central Albania we took samples from Graceni (EL)[**Longitude** 19° 57' 51" E; **Latitude** 41° 08' 58 " N and **Altitude (m. a.s.l)** 692] and Belshi (BE)[**Longitude** 19° 56' 47" E; **Latitude** 40° 54' 09 " N and **Altitude (m. a.s.l)** 136] sites. All sampling sites represent natural habitats of mixed forest stands of Turkey oak (*Q.cerris* L.) and Italia oak (*Q.frainetto* Ten.) in Albania. These forests stands are grown on cinnamon soils (brown soils) (Cambisols and Luvisols) developed from different parent materials like, clays, sand-allevrolite and limestone, flysch and colluvial deposits, and gypsum deposits.

The core sampling at first five sites was carried out during the period from October to November 2012, while the samples from Belshi area were taken in February 2014. In our sites, only Elbasan area is managed as high forest, so in this area we have tree with greater age and diameter.

Three stem discs (200mm) from the bole, middle and top of the stem were taken from each tree. (R1 for wood sample near tree base taken at 20cm height; R2 for wood sample taken at the middle and R3 for wood sample from upper crown). The stem discs were air dried. Discs are cleaned from the bark and any possible knock. For the each disks, tree-ring widths (TRW) were measured to the nearest 0.001 mm using a linear table, LINTAB and the TSAP-Win program, and were determined average of theirs. Also were determined the age for each disks (number of annual ring). (Fig.1)

Using a chainsaw, do some cutting, collecting necessary sawdust. In each case, we took care to remain unchanged correct proportion of sapwood and heartwood. Sawdust is riddled collected and stored fraction that runs the sieve 40mesh (0.400mm) and remains 60mesh sieve (0.250mm). When was needed was grinding in a hand- driven grinding mill. (T 257 cm-02).

The percentage of ash content was calculated on the basis of dry weight of original sample, after the sample was

ignited at muffle furnace at $575\pm 25^{\circ}\text{C}$. Carefully cleaned empty crucible with cover, and ignited them to constant weight in a muffle furnace at $575\pm 25^{\circ}\text{C}$. After ignition, cooled in desiccators and weighted the crucible with cover on the analytical balance. Transferred 3- 5 g of samples to the crucible, and it is set with lids removed, in an furnace, at a temperature no higher than about 100°C . The temperature is gradually increased to $575 \pm 25^{\circ}\text{C}$ so that the material is carbonized without flame. Burned material in furnace at $575\pm 25^{\circ}\text{C}$ for period of at least 3 hours a longer to burn off all the carbon. When ignition was completed as indicated by the absence of black particles, removed the crucible from the furnace, replaced the cover and allowed the crucible to cool somewhat. Then placed in desiccators and cooled to room temperature. Reweighted the crucible with ash and calculated the percentage of ash based on the moisture free (oven dried) weight of test specimen. . (T211-om 93) For each samples in parallel determined the moisture. (T 264 cm-07) Ash content was calculated by using following formula.

$$\text{Ash content \%} = (A/B) \times 100$$

Where, A= weight of ash (g) and B= weight of oven dried test specimen (g)

Result and discussion

Ash content values for samples analyzed by the study areas are presented in Figure 1. In each table shall contain information on the species of wood, the number of annual rings , the diameter of the disc at the time of cutting (cm) and the average of the annual rings width (TRW in mm) .

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Sample cod	specie	Diameter in cutting (cm)	Number of annual rings	TRW (mm)	Ash, dry basis (%)
T1R1U	frainetto	13.0	20	3.180	0.51
T1R2U	frainetto	7.0	12	2.438	0.65
T2R1U	frainetto	9.0	16	2.044	0.74
T2R2U	frainetto	5.0	12	1.665	0.75
T5r1U	frainetto	8.0	21	1.791	0.54
T8R1U	Cernis	11.2	20	2.443	0.54
T8R2U	Cernis	5.0	9	1.729	0.80
T9R1U	Cernis	8.0	13	2.589	1.00

a)

Sample cod	specie	Diameter in cutting (cm)	Number of annual rings	TRW (mm)	Ash, dry basis (%)
T1R1RR	Cernis	5.0	13	1.609	0.56
T2R1RR	frainetto	6.0	18	1.279	0.74
T4R1RR	Cernis	6.5	22	1.265	0.72
T4R2RR	Cernis	5.0	14	1.464	0.68
T5R1RR	frainetto	5.0	15	1.329	0.67
T6R1RR	frainetto	6.0	14	1.550	0.51
T7R1RR	Cernis	5.3	14	1.550	1.02
T8R1RR	Cernis	6.0	16	1.712	0.81
T11R1RR	Cernis	15.7	20	4.041	0.91
T12R1RR	frainetto	16.5	18	3.883	0.58
T12R2RR	frainetto	11.0	13	3.848	0.86
T12R3RR	frainetto	5.0	6	2.743	0.90

b)

Sample cod	specie	Diameter in cutting (cm)	Number of annual rings	TRW (mm)	Ash, dry basis (%)
T1R2DI	Cernis	5.0	13	1.809	0.91
T2R1DI	Cernis	8.5	11	2.722	0.80
T2R2DI	Cernis	3.8	6	2.512	0.97
T3R1DI	frainetto	6.7	24	1.847	1.01
T3R2DI	frainetto	3.6	7	2.223	1.07
T4R1DI	frainetto	8.0	27	2.090	1.19
T4R2DI	frainetto	4.0	7	2.421	1.25
T7R1DI	Cernis	22.0	22	4.490	1.39
T7R2DI	Cernis	14.0	18	3.552	1.46

c)

Sample cod	specie	Diameter in cutting (cm)	Number of annual rings	TRW (mm)	Ash, dry basis (%)
T1R1EL	Cernis	29.0	36	2.863	1.26
T1R2EL	Cernis	18.0	24	3.268	1.32
T1R3EL	Cernis	14.0	15	4.031	1.31
T2R1EL	Cernis	8.0	22	1.249	1.03
T3R1EL	frainetto	11.5	24	1.804	0.84
T4R1EL	Cernis	20.0	35	2.115	0.83
T4R2EL	Cernis	13.5	18	3.430	0.83
T4R3EL	frainetto	5.0	6	3.520	0.90
T5R1EL	frainetto	27.2	32	3.410	0.98
T5R2EL	frainetto	15.0	24	2.754	1.24
T5R3EL	frainetto	9.0	13	3.035	1.23
T6R1EL	frainetto	19.0	37	2.783	0.98
T6R2EL	frainetto	11.5	31	1.810	1.23
T6R3EL	frainetto	9.0	23	1.397	1.19

d)

Sample cod	specie	Diameter in cutting (cm)	Number of annual rings	TRW (mm)	Ash, dry basis (%)
T2R1BE	frainetto	8.0	15	1.845	0.73
T2R2BE	frainetto	5.5	14	1.191	0.84
T3R1BE	frainetto	11.0	16	2.756	0.83
T3R2BE	frainetto	7.5	13	1.822	0.90
T4R1BE	Cernis	13.8	16	2.789	0.81
T4R2BE	Cernis	8.5	11	2.457	0.83
T6R1BE	Cernis	8.5	16	2.195	0.83

e)

Figure 1. The data obtained for samples analyzed in all areas studied. (TRW =tree- ring width) a) for ULez; b)for Kukës; c) for Rrëshen ; d)for Dibër; e)for Elbasan and f)for Belsh

Making a regrouping of the obtained results for the total ash content of the base gaskets for analyzing samples from trees of *Q. cerris*, from all the studied areas we have: the average value for the total ash for this species *Mean of ash* = 0.92%; the maximum amount of ash *max* =1.39%, reached to T7R1DI; minimum value of ash *min*= 0.54% obtained to T8R1U, with a range of = 0.85% and standard deviation of ash *sd*= 0.20%.

There is a significant positive correlation between the ash content values in the trunk of the tree and the cutting diameter (*Q. cerris*), the coefficient of correlation $r = 0.57$ and significance level of $p = 0.021$.

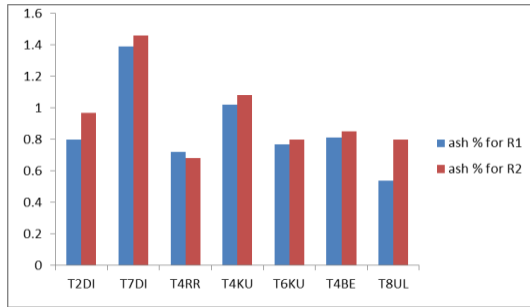
Making a regrouping of the results obtained for the total ash content of the base gaskets for analyzing samples from trees of *Q. frainetto*, from all areas of study have: the average value for the total ash for this species *Mean of ash* = 0.78%; the maximum amount of ash *max*=1.19%, reached T4R1DI; Minimum value of ash *min*=0.51% obtained to T1R1U, with a *range* of = 0.68% and standard deviation of ash *sd*= 0.19%

There was a significant positive correlation between the value of the contents of ash in wood and wood age (*Q. frainetto*), correlation coefficient of $r = 0.58$ and level of significance $p < 0.014$. A correlation between the content of ash and wood age and diameter reported to (Hakkila 1989) it stated that young trees tend to have a higher content of ash than mature trees but as we have said above all our trees considered young (≤ 37) (fig1 / e)

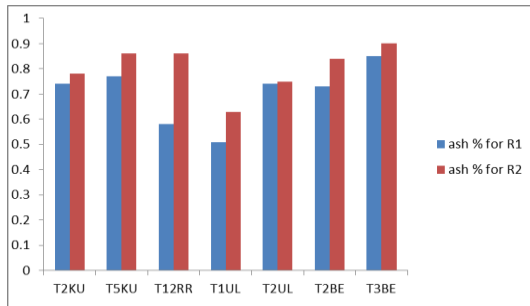
There was not found any significant correlation between the ash content in stem wood and the rate of growth rings (TRW). Such a result is given by (Mc. Millin 1969)

Roger C. Pettersen (1984) has summarized data for several species grown in different countries. Among them are presented data on some species of the genus *Quercus*, but not for our species since both are characteristic of Europe. However our values are compared with some of them.

Figure 2 presents a comparison of results obtained for the content of ash for disks R1 and R2 taken from the same tree a) of *Q. cerris* trees and b) the trees of *Q. frainetto*. As is apparent from the figure of ash content in disks R1 are lower than in those in R2.



a)



b)

Figure 2: Comparison between the ash content in the R1 and in the R2 a) for *Q.cerris* b) *Q.frainetto*.

About T1EL, T4EL, T5EL, T6EL and T12RR trees which have the greater diameter and the amount of sawdust, taken from their R3 disk that allows us to do parallel measurements, are made determinations even on the content of ash in R3 disk. In Figure 3 shows a comparison of the values of R1, R2 up to R3. As is apparent from Figure 3, ash content values between the gasket and the second and third are very close although the observed differences between the ash content in the R1 and R2.

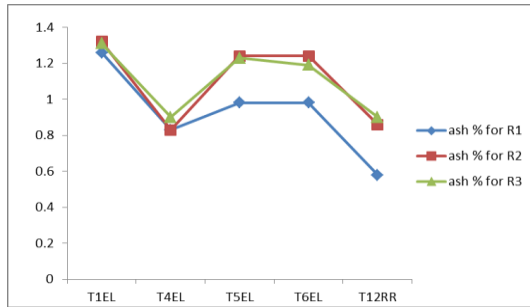


Figure 3: Comparison between the ash content in the R1, R2 and in the R3.

Similar results, to changes in the values of ash content in samples taken at different locations within the same tree, are reported for *Q. robur* by Krutul D. et.al. 2014 .

For samples of trees T5EL , T6EL and T12RR , where heartwood was formed too obvious , and in proportions that enabled us to separate from the sapwood, we defined the ash content in the heartwood . Figure 4 presents the ash content in stem wood and heartwood for these trees. As it seems the ash content in heartwood is significantly lower than in stem wood. Such an outcome result is reported also in other studies. (Krutul D. et.al. 2014; Krutul D. et.al 2010)

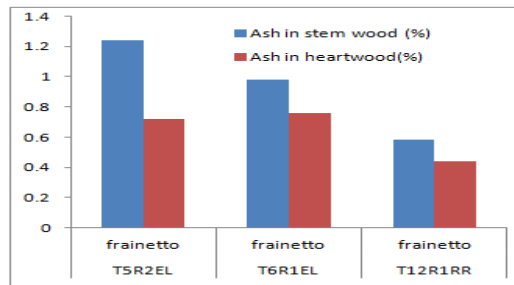


Figure 4. The ash content in the stem wood and in the heartwood.

For samples T1R1EL, T6R2, T11RR and T12R2RR was determined the content of the ash in the bark . As shown in Fig 5. Results for the bark are much higher than those for the stem wood (5-10 times) . Similar results have been reported in the

literature (Young 1971, Choong et al. 1976, Hattula and Johanson 1978, Harper and Einspahr 1980), where is stated that bark is generally higher in inorganic than in normal wood and the inorganic (ash) content can be as high as 13% and, in general, the inner bark contains more inorganic as compared to the outer bark.

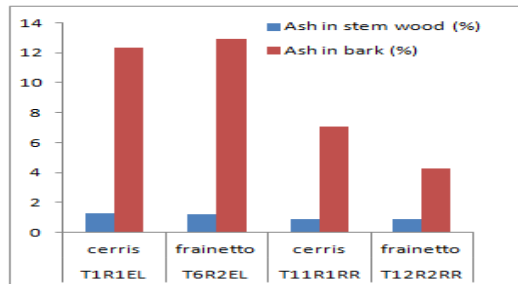


Figure 5. Ash content in the stem wood and in the bark.

Seeing relevant boxplots (Fig.6 and histograms (Fig 7) we see that the results for *Q.cerris* are higher and collected in a narrower range than the results for *Q.frainetto*.

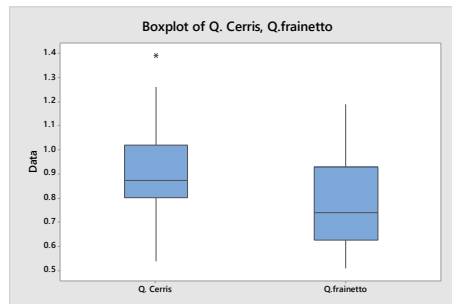
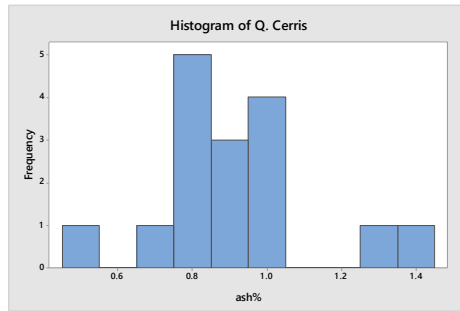
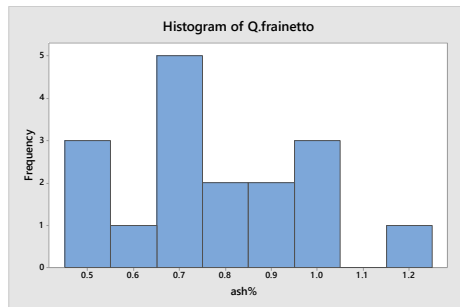


Figure 6. Boxplot for the content of ash in disks R1 for both species.



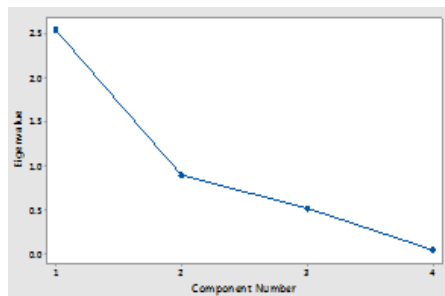
a)



b)

Figure7. The Histogram for the content of ash in disks R1 a) for *Q.cerris* b) for *Q.frainetto*

For the *Q. cerris* (for variables age, diameter in cutting, TRW and ash%) the first principal component had variance (eigenvalue) 2.5396 and accounted for 63.5 % of the total variance , PC2 and others have variances < 1.



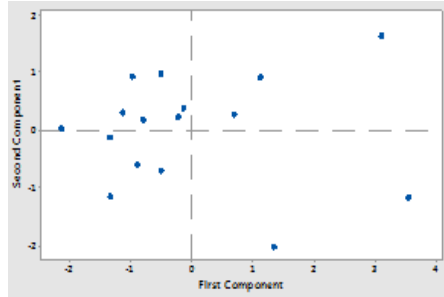


Figure8. The principal component analysis PCA for variables like age, diameter in cutting, TRW and ash% for *Q.frainetto* in R1 of the samples for all studied sites a) scree plot and b) score plot

For *Q.frainetto* (for variables age, diameter in cutting, TRW and ash%) the first principal component PC1 had variance 2.2261 and accounted for 55.7% of the total variance. The second principal component had variance 1.2329 and accounted for 30.8%. The second component could be thought as a contrasting level of diameter and TRW value with the ash content and the wood age.

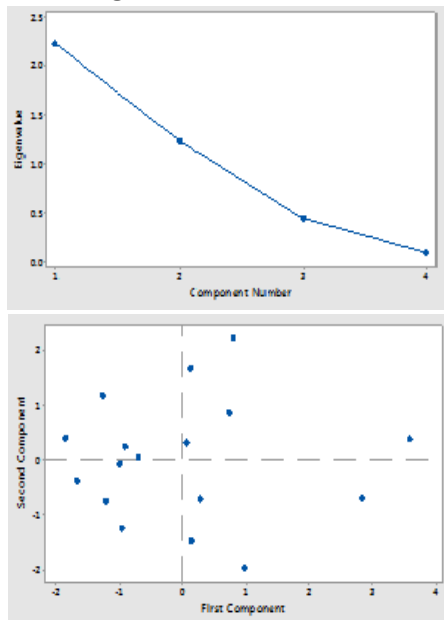


Figure9. The principal component analysis PCA for variables like age, diameter in cutting, TRW and ash% for *Q.frainetto* in R1 of the samples for all studied sites a) scree plot and b) score plot.

The dendrogram for *Q.cerris* data obtained from the hierarchical factor classification HFC analysis (Figure 10) has grouped the samples of R1 in two clusters. T8R1UL, T9R1UL, T4R1RR, T7R1RR, T8R1RR, T11R1RR, T3R1KU, T4R1KU, T6R1KU, T2R1DI, T2R1EL, T4R1BE and T6R1 BE samples have been grouped in the first cluster, while T7R1DI, T1R1EL and T4R1EL have been grouped in the second one.

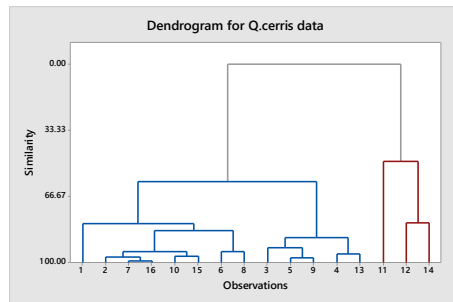


Figure10. The dendrogram created by HFC for *Q.cerris* data

The dendrogram for *Q.frainetto* data obtained from the HFC analysis (Figure11) has grouped the samples of R1 in two clusters. T5R1KU, T3R1DI, T4R1DI, T3R1EL, T6R1EL, T5R1EL and T3R1BE samples save been grouped in the first cluster while T1R1UL, T2R1UL, T5R1UL, T2R1RR, T5R1RR, T6R1RR, T12R1RR, T2R1KU, T8R1KU and T2R1 BE have been grouped in the second one.

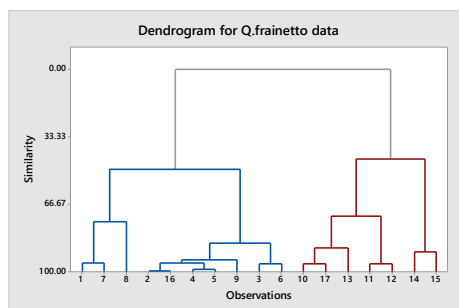


Figure11. The dendrogram created by HFC for *Q.frainetto* data

Conclusions:

Turkey oak (*Quercus Cerris* L.) and Italian oak (*Quercus Frainetto* Ten) are two wood species widely distributed in Albania .Oak forest are located near populated areas and they are often clear cut and managed with short rotation. This is the reason why they are so young. The ash content in the samples found *Q.cerris*.L ash % = 0.92 ± 0.20 and ten ash samples *Q.frainetto* % = 0.78 ± 0.17 . The content of ash in the heartwood was significantly lower than in stem wood. Ash content was found in the bark 5-10 times higher than in stem wood. The contents of the ash received in discs taken at near tree base 20cm height were lower than in the sample taken at the middle and at the top.

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