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THE SURFACE ANALYSIS OF FLEECE BY SEM AND THEIR ELEMENTAL CHARACTERISTICS OF MENEMEN SHEEP BREED

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ABSTRACT

In this study, fleece samples from a flock of Menemen sheep belong to a private enterprise were taken, and only the surface topography of the SEM and the fleece were examined. According to this examination, it was tried to find out what kind and how much elements exist within the fleece. This was tried to be determined through the SEM-EDX, XPS and ICP-OES analysis. The examined SEM images of Menemen sheep fleece seen that the cuticle surface was composed of scales shaped by the properly sorted cuticular cells and the cuticle cells were in the polygonal coronoid shape.

According to the analysis performed by ICP-OES method, it was found that the mean values of elements in the Menemen sheep fleece were respectively; Ca, 0.244 ± 0.006%; Na, 0.130% ± 0.008; Mg, 353.863 ± 13.369 mg/kg; K, 633.743 ± 65.295 mg/kg; Fe, 46.323 ± 7.847 mg/kg; Al, 45.054 ± 7.132 mg/kg; Si, 152.630 ± 17.626 mg/kg; Mn, 3.970 ± 0.318 mg/kg; Zn, 92.690 ± 2.073 mg/kg; Pb, 1.959 ± 0.364 mg/kg; Cu, 5.626 ± 0.289 mg/kg; Co, 0.120 ± 0.010 mg/kg; P, 150.033 ±3.728 mg/kg and Se, 0.070 ± 0.013 mg/kg. The elemental content of the fleece owns a special importance since it reflects the mineral status of the body thus could characterize as indicator in terms of the animal welfare.

Keywords: *Menemen Sheep Fleece, Element, SEM-EDX, ICP-OES, XPS.*

INTRODUCTION

The properties of the textile materials depend on the fibers used in the production while the quality of the fibers depends on some certain characteristics such as elasticity, strength and subtlety. These features in the fleece are proportional to the trace element contents (Özyol, 1990). Elemental analysis parameters possess a kind of indicator feature with animal welfare aspect and supply useful information in terms of the environmental conditions where the animal is located and the toxic effects may animal exposed to (Stevenson ve Wickham, 1976). Patkowska et al. (2009) reported that animal hair is a good bioindicator of air pollution, water quality, land and environmental condition, even much better as indicator than blood, urine or animal milk. Some certain number of disorders in sheep is associated with deficiency or excessiveness of trace element (Özyol, 1990). Bayşu et al. (1984); Combs et al. (1982), described that hair of mature animal is a metabolically active sequestered tissue and hence animal hair or mineral levels of fleece could be employed as indicator of the mineral status of the organism. Hilderbrand and White (1974) accounted that the measured mineral levels of the fleece or hair coat reflects the mineral status of the body in some certain amounts. Rashed and Soltan (2005) expressed Fe, Mn, Co, Ni as heavy metals and Cd and Pb as toxic metals, and they also reported that fleece is an effective monitoring tool in terms of/for identification of heavy metals and their amount in the roughage and in the land.

The advantages of analysis of animal hair in comparison to the blood and urine; i) several trace element concentrations highly exist in animal hair compared to other materials; ii) no special storage conditions are necessary; iii) in contrast to the blood, the animal hair is chemically homogeneous and in an inert position; iv) serum and urinary concentrations are both indicators for the acute situations and short-term response while concentrations in the animal hair is a retrospective indicator in terms of trace element amounts; v) sampling is easy (Laker, 1982, Bektas and Altintas, 2010). Maugh (1978) explained that the trace minerals are accumulated in animal hair or in the fleece at least 10 times higher than in the serum and urine and they also give information about the nutritional status; Noord and Zuki (1997) declared that Zn concentrations in sheep fleece are approximately 35-100 times higher than in the serum and plasma.

It has been known for so long that the major element content of the fleece is as follows: C (carbon), H (hydrogen), O (oxygen), N (nitrogen) and S (sulfur) (Özyol 1990), and the elemental composition of the dry wool fibre is formed of 50-52% C, 6.5-7.5 H, 22-25 % O, 16-17% N, 3-4% S (Kaymakçı and Sönmez 1992; Simpson and Crawshaw 2002). The minerals are effective in the development of fleece and include significant amount of Ca, K, Na, Zn Cu, Mn, Fe and Se (Lee & Grace, 1988). However, these elements like Cu, Zn, I and Se are directly influential on follicle growth and the fleece growth. S element is from the macroelements playing an important part in the fleece yield while Cu from the microelements has an important role in wool fiber quality of the fleece. Copper deficiency emerges due to the high level of Mo and S either in sheep ration, and leads to a decrease in crimp, strength and brightness of the fleece as a result of the fleece depigmentation. The deficiency of both Zn and Se causes a notable decline in the fleece growth (White et al., 1994).

Scanning with electron microscope (SEM) has found an important usage area especially in the textile industry on the examination of the cuticular surface. Chauhan et al., 1981; Beninate et al., 1981and Kassenbeck et al. (1975) found impact of treating fleece with different agents and the changes that happened in various processes, which were applied to the fleece (degradations in proteins and cell losses because of breakdown in the fleece fiber); Goudarzi et al. (2008) determined, with the use of SEM method, that the enzymes used for wool treatment affect the scale layer of the wool. Koestler et al. (1985) and Carr et al. (1986) identified concentrations percentage of some various elements in the fleece by using EDX (Energy Dispersive X-ray). Qi et al. (1994) reported also that observing cuticular surface with scanning electron microscope plays a significant role. Broeck et al. (2001) stated that SEM method is a quick and useful method in the examination of animal hair types by using three-dimensional imaging and in the classification of the animal hair types by taking the longitudinal and circular image of the cuticle diameter and topographic properties of the animal hair.

XPS (X-ray Photoelectron Spectroscopy) is a surface analysis technique that enables identify the changes in the current element concentrations located in epicuticula layer on the surface of the wool up to a depth of 3 nm (Carr et al., 1986). Walawska et al. (2006) studied physico-chemical changes on the surface of wool after enzymatic processes and reported that the changes in the element concentration on the surface can be compared with the help of XPS.

Gabryszuk et al. (2010), Lesniewska et al. (2003), Aydın (2008), Hawkins and Ragnarsdottir (2009) determined the mineral elements in some fleece samples by employing ICP-OES.

As the electron microscopes are not extensively used on the fleece studies and elemental analyzes of the current sheep breeds in Turkey, this situation makes this study unique. It was aimed from this study to determine the elements content of the fleece in different ways.

MATERIALS AND METHODS

This study was performed on the fleece samples taken from a flock of Menemen sheep, belong to a private enterprise. To start the study, SEM images of fleece fibers were taken with 2500 times magnification at the 20.0 kV standards. In following step for this study, only the surface topography of the fleece was examined by SEM. SEM-EDX and ICP-OES and MS analysis were conducted on a total number of 30 fleece samples which incuded 10 fleece samples to represent the young age group ranged from 6 months to 1.5 years old, 10 fleece samples to represent middle-aged group ranged from 2 and 3.5 years old and 10 fleece samples representing the old group ranged from 4 and 5+ years old. One of them was used in the preliminary study of the XPS analysis. The elemental analysis of the fleece was conducted by SEM-EDX device and the other procedures concerning the SEM image of the fleeces were performed at Afyon Kocatepe University, Technology Applications and Research (TUAM) Labaratory. However, XPS and ICP-OES and MS analysis along with elemental analysis were carried out at Middle East Technical University (METU) Central Laboratory**.** Yet, it was decided that analysing with XPS device is not a suitable way for this study since only the percentage amounts of C and O elements could be detected by XPS analysis. Thus, proceeding analysis with this method was ended. In the ICP-OES analysis, Na, K, Mg, Ca, Fe, Al, Si, and Zn elements were found out while Mn, Co, P, Cu, Se, Pb elements were determined in the ICP-MS analysis.

In the analysis of data concerning the elemental analysis of the fleece through SEM-EDX and ICP-OES, one-way variance analysis (one way ANOVA) was used for the comparison of each variable according to age groups. The Duncan Test which is one of the multiple range tests and is used in the binary comparisons was applied in case of significant differences among groups.

RESULTS AND DISCUSSION

As the SEM images of Menemen sheep fleece are examined, it is seen that the cuticle surface was composed of scales shaped by the properly sorted cuticular cells and cuticle cells were in the polygonal coronoid shape (Fig. 1).

According to Table 1; the general average of C, N, O, S, K, Na, Mg, Ca, Cu & Al elements by the SEM-EDX technique found to be as follow: 20.54 ± 0.50%, 22.00% ± 0.35%, 48.60 ± 0.56%, 6.90 ± 0.12%, 0.12% ± 0.03%, 0.70 ± 0.04%, 0.42 ± 0.02%, 0.19 ± 0.02%, 0.12 ± 0.01, 0.74 ± 0.03%, respectively. As a result of the statistical studies, it is seen that S element in young age group has a lower value than S value in the old and middle age groups (Table 1). It was determined that C, N, O, K, Na, Mg, Ca, Cu & Al elements did not vary according to age groups. In the SEM-EDX analysis, the Fe, Si, Mn, Zn, Pb, Cu, Co, P & Se elements that were expected to be presented in the fleece were not detected.

As seen in Table 2, the Ca, Mg, Mn & Pb levels done by ICP technique in middle-aged fleece group was found to be the highest while the lowest was in the young age fleece group (middle age group> old age group> young age group). The level of Na in young age fleece group was the lowest whereas it was the highest in the old age group fleece (old age group> middle age group> young age group). K, Zn, Cu & P levels for young age fleece group was found to be the highest while it was the lowest in the old age fleece group (young age group> middle age group> old age group). Se level for the young age fleece group was found to be the highest while it was found to be the lowest in the middle age fleece group (young age group> old age group> middle age group

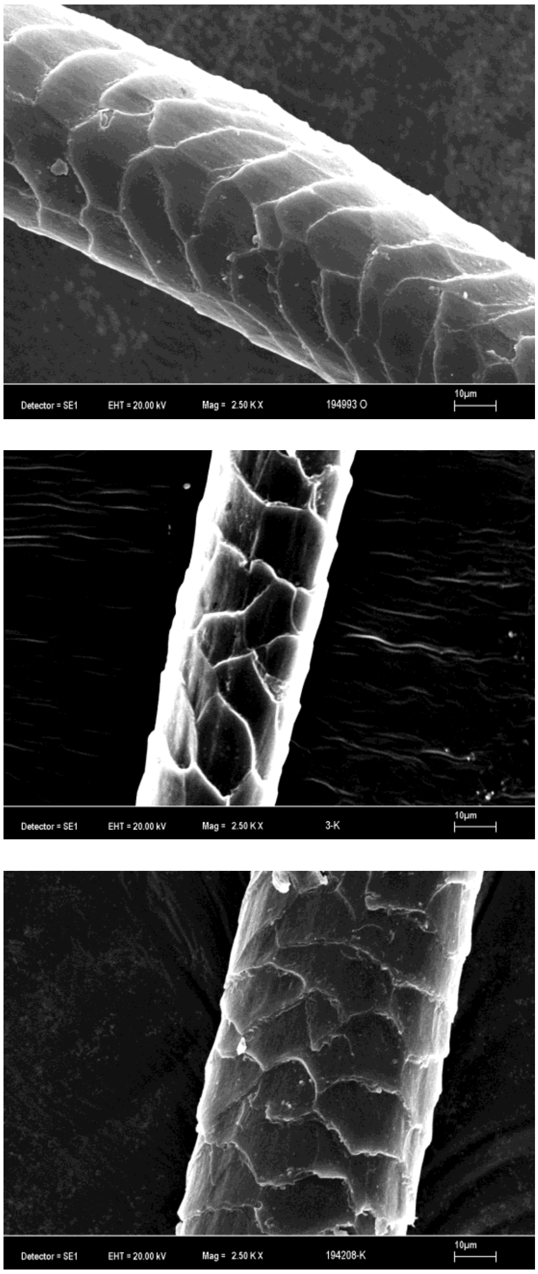

Figure 1. SEM Image of the fleece fiber in Menemen Sheep

In the same table, the concentrations of Ca, Na, Mg, K, Mn, Zn, Pb, Cu, P and Se elements varied among age groups ($p<0.05$). No statistically significant difference were detected among groups in terms of Fe, Al, Si and Co elements (Table 2).

According to the information provided in Table 2, the general average of Ca, Na, Mg, K, Fe, Al, Si, Mn, Zn, Pb, Cu, Co, P and Se elements found out were respectively 0.244 ± 0.006%, 0.130 ± 0.008%, 353.863 ± 13.369 mg/kg, 633.743 ± 65.295 mg/kg, 46.323 ± 7.847 mg/kg, 45.054 ± 7.123 mg/kg, 152.630 ± 17.626 mg/kg, and 3.970 ± 0.318 mg/kg, 92.690 ± 2.073 mg/kg, 1.959 ± 0.364 mg/kg, and 5.626 ± 0.289 mg/kg, and 0.120 ± 0.010 mg/kg, 150.33 ± 3.728 mg/kg, and 0.070 ± 0.013 mg/kg.

Accordingly, images obtained by the SEM technique offer a good help since it make it possible to:

i) clarify some controversial forensic medicine cases, ii) observe the changes by SEM, which appear in the morphological structure of the fleece during race determination of the fleece fiber, animal

ii) breeding and the adaptation of the animal, iii) determine the suitability of the fleece fiber to the intended usage areas depending on the developing technology, (insulation, etc.), iv) observe the changes or losses by SEM, which come out as a result of the fleece's exposition to a variety of procedures in different ways in textile industry, v) examine the cuticle layer of the fleece fiber, yield results shortly and enable to display three-dimensional imaging, vi) measure the subtility of fleece fiber, the scale number on the surface and the height of the scale by SEM (Turan, 1999; Goudarzi et al. 2008; Leonte et al. 2011; Yıldız et al. 2004; Broeck et al. 2001; Varesona et al. 2005; Qi et al 1994).

iii) In the elemental analysis of the study, by SEM-EDX, 20.54 ± 0.50% carbon, 22.00 ± 0.35% nitrogen, 48.60 ± 0.56% oxygen 6.90 ± 0.12% sulfur were obtained. The wool macromolecules include 1 amino 2 carboxyl group (glutamine acid, asparagine acid) or amino acids containing hydroxyl in its structure and polar group (such as serine), free carboxyl,-COOH, OH, or polar groups in the macromolecule (Harmancioglu, 1974, Plant, 2006; Sarı, 1982). The reason why O content is more than C content is because of the free hydroxyl, carboxyl and polar groups on the wool surface. Moreover, the reason why S level in wool is high in stems from the reason that S content of the animal hair in the cuticle layer is higher compared to the cortext and medulla (Körlü ve Altay, 2009; Sarı, 1982). In addition, this situation may be defined by the fact that SEM-EDX is able to make a semi-quantitative anaylsis.

C, O, N, S, Na, K, Mg, Ca, Mn, Fe, Co, Cu, Zn, Al, Si, P, Se and Pb elements were analyzed by XPS device at METU (Middle East Technical University), Central Laboratory, and the C element was identified as 83.70% and the O element was identified as 16.30% as a result of the overall scan. The reason why neither nitrogen nor sulfur was found according to the analysis result is because lanolin was not removed well from the wool in the course of wool washing, and it is predicted that probably the grease layer on the surface was analyzed. However, the XPS device is widely used in the textile industry for the determination of surface characterization of the raw materials, (Carr et al. 1986, O'Connor, 1992; Walawska et al., 2006; Seventekin and Özdogan 2008).

Ca level in Menemen sheep breed was measured as 0.244 ± 0.006% (2.440 mg/kg) by ICP-OES methods similar to the values determined by Patkowska et al. (2009) as 1.790-2.900 mg/kg. However, this value is less than the value found by Aydın (2008) (0.41-0.66%) for the two-months old male lamb flecees. In addition, the level is less than the values found by Sahoo and Soren (2011) as 323.000 mg/kg and by Hutchinson and Symington (2011) in Coswold, Shropshire, Dorset & Shetland breeds respectively as 74.000-316.000, 82.000-101.000 111.000-159.000, 151.000-326.000 mg/kg. Compared to other studies, the current differences in the level of Ca are thought to arise due to the sheep race, sheep age, sheep gender and environmental conditions (supply, care & vegetation).

The Na level was found as 0.130 ± 0.008 % (1.300 mg/kg) in Menemen sheep fleece which was less than the values found as 1.486-2.165

mg/kg, 63.000 mg/kg, 3.000 mg/kg, 0.28-0.37% by Patskowska et al. (2009) , Sahoo and Soren (2011) Burns et al. (1964) , and Aydin (2008), respectively.

The Mg level was found as 353.863 ± 13.369 mg/kg (0.035 %) in Menemen sheep fleece which was higher than the values found as 59.000 mg/kg by Sahoo and Soren (2011). Moreover, the findings of this study also was higher than the findings of Hutchinson and Symington (2011) in which they detected Mg level as 11.000-41.000 mg/kg 12.000-31.000 mg/kg, 19.000-30.000 mg/kg, 22.000-39.000 mg/kg in Cotswold, Shopshire, Dorset & Shetland breeds, respectively. On the other hand, it was lower than the values found as 0.09-0.13 % by Aydın (2008).

Burns et al. (1964) & Healy and Zieleman (1966) reported that breed, pasture-keel and the season are effective in the mineral content of the fleece whereas Özyol (1990) believed that at the time that Ca, Mg and Mn element concentrations decrease in the fleece, the fiber subtility lessens, too.

The K level found as 633.743 ± 65.295 mg/kg (0.063%) is similar to the value found by Patkowska et al. (2009) as 643.755 mg/kg, while it is higher than the values found by Aydin (2008) as 0.03 - 0.06%.

Regarding Fe level (46.323 ± 7.847 mg/kg), it was similar to the values 22.030-513.170 mg/kg found by Patkowska et al. (2009) and 42.000 mg/kg found by Sahoo and Soren (2011). Fe level was found higher than the values determined by Symington Hutchinson (2011) in Cotswold, Shropshire, Dorset and Shetland sheep breeds respectively (6.000-19.000, 14.000-22.000, 9.000-31.000 and 9.000-25.000 mg/kg). On the other hand, Fe level was detected to be lower than the values found by Bektas and Altintas (2010) in Merinos and Ile de France crossbred fleece as 107.690 ± 87.470 and 94.390 ± 65.910 mg/kg. Patkowska et al. (2009) explained that these differences in the level of Fe are due to the element content of the land and nutrient intake of animals in the grassland.

Miller (1985) expressed that Mg and P macro elements and Zn, Fe, Cu, and Se trace elements are effective against infection; and considered that resistance to diseases decreases especially in the absence of trace minerals so that immune defense system is impaired. On the basis of this information, it can be expressed from data obtained in this study that health status of animals is well except for Se element.

The Al level was found as 45.054 ± 7.132 mg/kg in Menemen sheep fleece which is close to the level found by Patkowska et al. (2009), as 53.650-620.830 mg/kg; while it was lower than the level found by Lewniewska et al. (2003) as 82.070 mg/kg in Polish fleece and as 74.170 mg/kg in Australian fleece. Regarding Si level, it was found as 152.630 ± 17.626 mg/kg, which is lower than the value found by Burns et al. (1964) as 230.000 mg/kg.

The Mn level was found as 3.970 ± 0.318 mg/kg which is similar to the values found by Sahoo and Soren (2011) as 3.400 mg/kg; however, it is higher than the values found by Lesniewska et al (2003) in Australian fleece as 2.148 mg/kg, but lower than the values they found in Polish fleece as 7.903 mg/kg. Patkowska et al (2009) and Aydın (2008) reported that the differences observed in Mn level depended on the environmental conditions and animal race while Altıntaş (1990) expressed that 70.000 mg/kg Mn level in fleece is the critical level for toxication. In light of this information, it may be considered that Mn level among the studied sheep is not at the toxic degree.

The Zn level was found as 92.690 ± 2.070 mg/kg, which was higher than the values found by Lesniewska et al. (2003) in Polish and Australian fleece as 70.360 mg/kg and 89.040 mg/kg and Patkowska et al. (2009) as 73.620-88.800 mg/kg. Moreover, the findings of this study also higher than the values found by Hutchinson and Symington (2011) in Coswold, Shropshire, Dorset and Shetland sheep breeds respectively as 15.800-24.100 mg/kg, 18.300-25.700 mg/kg, 20.800-30.500 mg/kg and 16.300-23.200 mg/kg. On the other hand, it is lower than the values found by Sahoo and Soren (2011) as 114.000 mg/kg. Stevenson and Wickham (1976) pronounced that the type of birth did not affect the Zn level of the fleece whereas age, gender and the density of settlement were effective. The Zn level in 2 years old fleece is less than the level in 4 years old fleece, and it was figured out that

Table 1: The Element Contents of Menemen Sheep Fleece by Age Groups determined by SEM-EDX

Age	N	C (%)	N (%)	O (%)	S (%)	K (%)	Na (%)	Mg (%)	Ca (%)	Cu (%)	Al (%)
Young age group	10	21.03±1.04	22.87±0.65	48.68±1.06	6.43±0.24 (a)	0.22±0.06	0.59±0.05	0.34±0.05	0.16±0.01	0.15±0.21	0.63±0.80
Middle age group	10	21.34±0.56	21.47±0.60	47.39±0.78	7.27±0.19 (b)	0.12±0.07	0.78±0.07	0.49±0.03	0.12±0.07	0.10±0.03	0.78±0.02
Old age group	10	19.24±0.86	21.66±0.55	49.73±1.00	7.01±0.07 (b)	0.03±0.02	0.72±0.08	0.44±0.06	0.21±0.06	0.12±0.02	0.80±0.04
P		ÖD	ÖD	ÖD	0.011	ÖD	ÖD	ÖD	ÖD	ÖD	ÖD
Mean	**30**	**20.54±0.50**	**22.00±0.35**	**48.60±0.56**	**6.90±0.12**	**0.12±0.03**	**0.70±0.04**	**0.42±0.02**	**0.19±0.02**	**0.12±0.01**	**0.74±0.03**

Table 2. The Element Contents of Menemen Sheep Fleece by Age Groups determined by ICP-OES

Age	n	(Ca) (%)	Na (%)	Mg(mg/kg)	K (mg/kg)	Fe (mg/kg)	Al (mg/kg)	Si (mg/kg)
Young age group	10	0.221±0.006 (a)	0.111±0.015 (a)	309.210±17.516 (a)	865.800±114.111 (a)	34.440±3.706	35.980±7.185	156.300±23.720
Middle age group	10	0.269±0.010 (b)	0.115±0.005 (a)	391.780±18.857 (b)	576.710±107.537 (ab)	70.700±20.009	64.840±14.565	193.370±31.162
Old age group	10	0.243±0.012 (ab)	0.164±0.014 (b)	360.600±26.060 (ab)	458.720±82.929 (b)	33.830±9.062	34.342±12.753	108.220±32.627
P		0.010	0.012	0.033	0.026	ÖD	ÖD	ÖD
Mean	**30**	**0.244±0.006**	**0.130±0.008**	**353.863±13.369**	**633.743±65.295**	**46.323±7.847**	**45.054±7.132**	**152.630±17.626**
		Mn (mg/kg)	**Zn (mg/kg)**	**Pb (mg/kg)**	**Cu (mg/kg)**	**Co (mg/kg)**	**P (mg/kg)**	**Se (mg/kg)**
Young age group	10	2.566±0.115 (a)	100.010±3.685 (a)	0.816±0.206 (a)	7.208±0.490 (a)	0.125±0.018	164.250±5.316 (a)	0.111±0.023 (a)
Middle age group	10	5.393±0.591 (b)	89.700±2.699 (b)	2.960±0.817 (ab)	4.967±0.352 (b)	0.121±0.020	146.380±5.661 (b)	0.025±0.013 (b)
Old age group	10	3.952±0.412 (c)	88.360±3.413 (b)	2.101±0.557 (b)	4.703±0.151 (b)	0.113±0.015	139.470±6.143 (b)	0.075±0.023 (ab)
P		0.000	0.037	0.048	0.000	ÖD	0.014	0.023
Mean	**30**	**3.970±0.318**	**92.690±2.073**	**1.959±0.364**	**5.626±0.289**	**0.120±0.010**	**150.033±3.728**	**0.070±0.013**

$p<0.05$ *P: ANOVA* a,b, c: The difference is remarkable among the groups including the different letters in the same column.

the Zn level in the fleece of the dense settlement is lower than the level in the control group.

The Zn levels in young age group (6 months and 1.5 years) was determined to be higher than the middle age group (2-2.5 and 3- 3.5) and older group (4-4.5, and 5+). Scott (1991) reported that the normal Zn content of sheep fleece changed from 35.000 to 195.000 mg/kg and it was connected to the element content of the ration and the physiological state of the animal. According to the results obtained from this study and the available information in literature, it is realised that the Zn concentration varies depending on race, gender, age, region and density of settlement.

The Cu level, found as 5.626 ± 0.289 mg/kg, is among the values found by Noordin and Zuki (1997) in sheep fleece grown under three different management system in four different sheep farms as 4.600 ± 1.300, 11.800 ± 6.800, 4.700 ± 0.800 and 9.900 ± 6.500 mg/kg; and is among the values detected by Patkowska et al. (2009) as 5.300 to 10.300 mg/kg. However, the values are higher than those found out by Lesniewska et al. (2003) in Polish fleece as 4.412 mg/kg and Sahoo and Soren (2011) as 2.900 mg/kg. Patkowska et al. (2009) reported that the differences observed in the Cu content in sheep fleece is due to the element content of the diet and added that the low copper levels in the blood can be effective in the reduction of element content of the fleece.

Önder and Keçeci (2003) stated that the addition of copper and zinc to the ration increased the copper and/or zinc levels, yet the addition of copper to the rations of the animals led to a decrease in the elasticity of fleece fibers. White et al. (1992) reported that addition of minerals to the ration significantly increased the productivity and strength of the fleece.

Ramirez-Perez et al. (2000) reported that the race has an effect on copper concentrations in the fleece and that Cu concentration in the fleece may vary depending on its concentration in the ration and it was stated that the low level of copper in the fleece might be a reflection of copper level detected in the blood below normal level. In the present study, it was seen that Cu level in Menemen sheep fleece is similar to the acknowledgement inliterature. Köksal (2007) stated that the need for copper in sheep is among 5.000-10.000 mg/kg values, meanwhile Köksal (2007) reported that the tolerance to copper in sheep is not at a critical level, which was identified as 25.000 mg/kg.

Bektas and Altintas (2010) expressed that copper plays an important role in the course of undulation, and that curves and softness of the fleece may disappear in the event of copper absence and be toughened, in that the quality of fleece decreases. Healy and Zieleman (1966) put forward that variation of copper and zinc content of the fleece is connected to land while O'Mary et al. (1970) expressed that copper intake affects copper level in the hair of sheep fleece and cattle during feeding. Noordin and Zuki (1997) reported that Zn concentration varied according to race, age, gender and region. Sreenivasa et al. (2002) and Hawkins and Ragnarsdottir (2009) informed that there were differences in the unwashed sheep wool among the Cu, Zn and Mn content samples due to external contaminations and that trace element concentration reduced owing to washing. Cu, Zn and Mn content, fleece age, distance of cut from skin and washing procedure have an effect on the washed sheep fleece.

Reis and Sahlu (1994) stated that particularly copper and zinc are from the trace elements essential for the growth of the fleece; and the fleece becomes weak with losses in the scales of the fleece come out in the case of deficiency and/or imbalance of these elements. McDowell (1992) pointed out that keratinization and pigmentation disorders in mature animals appear in the event of copper deficiency, and it ends up with depigmentation in the animal hair and degradation in the quality of the fleece.

Bayşu et al. (1984) mentioned that enzootic ataxia is occured in lambs due to copper deficiency; and it results in financial losses and the incidence of the disease varies by region. They reported that this disease is diagnosed at the blood-copper level of 50 μg/dl and when the copper level of the fleece fall below 4.500 mg/kg. Thus, the Cu value found as 5.626 ± 0.289 mg/kg in Menemen sheep fleece is regarded as an indicator that it is not at a critical degree for the disease.

The Pb level found as 1.959 ± 0.364 mg/kg is higher than the value found by Aydın (2008) in lamb fleece as 0.420-1.880 mg/kg, while it is lower than the value found by Patkowska et al. (2009) as 2.320-2.590 mg/kg. Crivineanu et al. (2010) found out the Pb level in the fleece of sheep graze in 5 seperate pastures distant from different traffic routes in Greece for a period of 3 and 6 months. The results after 3 and 6 months are respectively 0.170-3.530 mg/kg and 0.280-5.310 mg/kg.

Hristev et al. (2008) detected that environment has a significant impact on the Pb content of sheep fleece, and found out the values in Pb-contaminated, washed and unwashed sheep fleece respectively as 8.150 ± 1.830 mg/kg and 15.300 ± 2.430 mg/kg. Özyol (1990) and Maugh (1978) stated that concentrations of toxic elements in a fleece give information about environmental pollution and this information could be used in monitoring environmental pollution.

The Co level, found as 0.120 ± 0.010 mg/kg, is less than the values found as 0.590-1.520 mg/kg, 0.650-2.310 mg/kg, 1.220-2.690 mg/kg by Aydin (2008), Patkowska et al. (2009), Bektas and Altintas (2010) respectively. Patkowska et al. (2009) reported that the differences observed in the Co content of sheep fleece are due to the degree of environmental pollution or the origins of country.

The P level, found as 150.033 ± 3.728 mg/kg, is among the values found by Patkowska et al. (2009) as 148.000-284.000 mg/kg and Healy and Zieleman (1966) as 117.000-151.000 mg/kg, whereas it is higher than the values found by Sahoo and Soren (2011) as 120.000 mg/kg.

The Se level, detected as 0,070 ± 0,013 mg/kg, is alike the values found by Hutchinson and Symington (2011) in Coswold sheep breed as 0.040-0.160 mg/kg, in Shropshire sheep breed as 0.040-0.140 mg/kg, in Dorset sheep breed as 0.020-0.070 mg/kg and in Shetland sheep breed as 0.020-0.120 mg/kg. On the other hand, the level is higher than the values found by Antunovic et al. (2010) (from 0.006 ± 0.002 to 0.060 ± 0.006 mg/kg). The Se level is lower than the values determined by Bektaş and Altıntaş (2010) in Merinos and Ile de France crossbred fleece (from 7.070 ± 4.960 to 3.750 ± 1.890 mg/kg) and by Sahoo and Soren (2011) as 0.510 mg/kg. Bektaş and Altıntaş (2010) highlighted that selenium has a part in the formation of the wool quality. Wuyi et al. (1987) reported that Se concentration of the fleece is related to the Se concentration in lands and plants. Altıntaş (1990) expressed that 0.250 mg/kg Se level is the critical level for insufficiency in fleece, and reported that 10.000 mg/kg is the toxic level. Based on this information, it can be concluded that Se level found as 0.070 ± 0.013 mg/kg in Menemen sheep fleece is not at the toxic level but it is at the critical degree for insufficiency. According to the results of other studies, the differences observed in the values of mineral level in the fleece could be associated with the differences in mineral levels of animals' daily intake.

According to the examined literature, it was realised that race, age, gender, region, settlement density, vegetation, physiological status of the animal, diseases, nutritional status, the element content of land and whether the fleece was washed or unwashed are influential in the mineral levels of the fleece (Özyol, 1990, Healy and Zieleman, 1966; Burns et al. 1964; Patkowska et al., 2009, Scott, 1991; Noord and Zuki, 1997).

Combs (1987) reported that mineral level of the animal hair is affected by sex, age, hair color, body area and the contamination except for nutrion; accounted that the differences in the amount of perspiration due to the ambient temperature leads to differences in the level of trace element of the hair; and added that the level of copper in the animal hair is related to copper deposition in the liver.

ICP-OES or ICP-MS technique is a fast and reliable method for determination of the contents of element. Unlike other surface analysis techniques, it provides us with a chance to make a more precise and reliable measurement, and it enables us to identify the elements that cannot be identified by other surface analysis techniques. It is able to provide results in percentage (%) and mg/kg level. However, the determination of C, N, O & S elements that are in the nonmetallic groups cannot be made.

As mineral levels of Menemen Sheep Fleece that were determined by ICP-OES technique are comparable with other studies, it was found out that Ca, Na, Mg, K, Cu & Fe elements are generally higher in Menemen Sheep Fleece and Mn, P, and Zn elements are similar to quite higherwhile Se level is lower. Under the light of the information gained, it is thought that the ration program needs to be reviewed in order to make up the Se element deficiency, which is effective on the growth and the quality of the fleece.

CONCLUSION

It was determined that ICP-OES method, which is one of the methods employed in the elemental analysis of the Menemen sheep fleece, provides more advantageous and reliable results than SEM-EDX and XPS methods. It is possible to identify the contents of many elements in a short time period. Although, XPS and SEM-EDX methods are appropriate for the surface analysis and identification of the content of element, considering the results, particularly obtained by EDX method, it was frazed that element analysis conducted with this method are not precise and reliable.

Giving importance to the fleece in terms of livestock product and textiles as industry material, it can be expressed that a more rapid progress will be achieved if these sectors act hand in hand on the works that finally meet the needs of the industry.

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