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Variation of elemental concentration in leather during post-tanning operation using energy dispersive X-ray fluorescence spectroscopy: principal component analysis approach

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ABSTRACT

Leather processing employs a series of heavy chemicals that are detrimental to human health and environment at different stages of tanning. Determination of the elemental concentrations becomes complex especially using the conventional techniques since they involve tracking individual elements at different stages of leather-making processes. The study investigated the effect of crusting operations on the elemental concentrations using energy dispersive X-ray fluorescence (EDXRF) and principal component analysis (PCA). The spectral measurements of the post-tanned samples were carried out in vacuum using EDXRF-Rigaku NEX CG. The concentrations of elements were determined by advanced FP (fundamental Parameter) software-RPF-SQX (Rigaku Profile Fitting-Spectra Quant X) software. The abundance of the elements in the leather crusts was in the order Cr>S>Na>Cl>Al>Si>Ca>V>K>P>Zr>Zn>Fe>Mn>As>Ti>Cu>Pb>Ni>Ga > Br > Hg. The concentration levels for the majority of the elements in the crusts were higher than the recommended safe extractable levels for leather. Combination of EDXRF and principal component analysis in this study has shown potential in the leather industry to monitor the chemical concentrations. A combination of Cu and RX9 secondary targets exhibited sufficient and excellent excitation efficiency for detection of the majority of elements in leather crusts. The valuable tracers for classification in the crusting operations are Cr, S, Cl, P, V, K, Mn and Zn. Retanning process increases S and Cu whereas levels of Cl decrease in the crusts. Dyeing and Fatliquoring processes raise the concentration levels of S while decreasing the Cl level.

1. Introduction

Leather processing is based on the transformation of putrescible hide/skin into physically and chemically stable raw material that meets high-end customers' needs [1,2]. The transformational processing goes through pre-tanning, tanning, post-tanning and finishing

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Supplemental data for this article can be accessed here.

operations, which heavily use acids, bases, enzymes, salts, dyes and fatliquors among others [2–4]. Potentially, the chemicals used in these processes amount to significant environmental pollution through effluents and solid wastes and also render the final leather risky to both environment and human health [5,6]. Similarly, the presence of some chemicals and conditions during these operations, such as pH modification, facilitate and accelerate the formation of other pollutants in leather such as radical formation: hexavalent chromium [4,7–11]. The concentration levels of some of the elements in leather and its products is a concern to regulatory bodies of public health and environment [4,7–15]. It is in the interest of the leather industry to produce quality leather that complies with international standards of chemical element concentrations. This will minimise the rejection rates of leather products at the international markets and safeguard the environment and human health [16,17]. A holistic approach by the industry should involve a comprehensive evaluation of the leather processing in terms of chemical contribution to the final leather to enhance environmental monitoring.

A number of studies have been carried out to determine the chemical properties of leathers and tannery effluents such as chemical oxygen demand, total dissolved solids, nitrogen, chromic oxide content, total organic carbon, volatile fats and extractible fatty matter contents [10,18–24]. Other studies have focused on hazardous elements in parchments and finished leather using XRF, inductively coupled plasma optical emission spectroscopy (ICPOES) and Instrumental Neutron Activation Analysis (INAA) techniques [10,14,25,26]. Determination of trace elements using ultrasonic nebulisation and axial view-ICP OES and toxic metals using wavelength dispersive X-ray fluorescence (WDXRF) and ICP OES in chrome-tanned leathers has been documented [27,28]. Although extensive work has been done in this area of chemical properties of leather and the possible environmental pollution of tannery discharges, information on the effect of leather-making processes on the elemental composition of the actual leather is scanty. Therefore, this study focused on investigating the elemental concentrations of leather crusts along the course of the post-tanning operations using EDXRF NEX CG coupled with fundamental parameter quantification technique. The EDXRF NEX CG employs polarised excitation that offers a lower limit of detection and also high analytical precision offered by the silicon drift detectors. The close-coupled Cartesian Geometry (CG) optical kernel increases the peak to background. Additionally, EDXRF does not require simple sample preparation which minimises cost and time unlike other conventional techniques such as ICP OES which require tedious and expensive processes of sample preparation such as acid digestion and extraction. The PCA of data was done using Origin 2018 to help identify the possible provenance within the crusting operations and prior operations.

2. Materials and methods

2.1. Leather tanning

One fresh raw cowhide was commercially procured from a slaughterhouse, weighed and soaked in 200% water and 1% detergents by weight for 30 min to remove dirt. The pelt underwent processing to chrome tanning stage as described in Nalyanya et al. [29] at Kenya Industrial Research and Development Institute-Nairobi. The wet blue was fixed using formic acid and cut into two identical pieces along the backline. One-quarter of one piece was cut out within the butt area and labelled as a tanned sample (T) as shown in Figure 1.
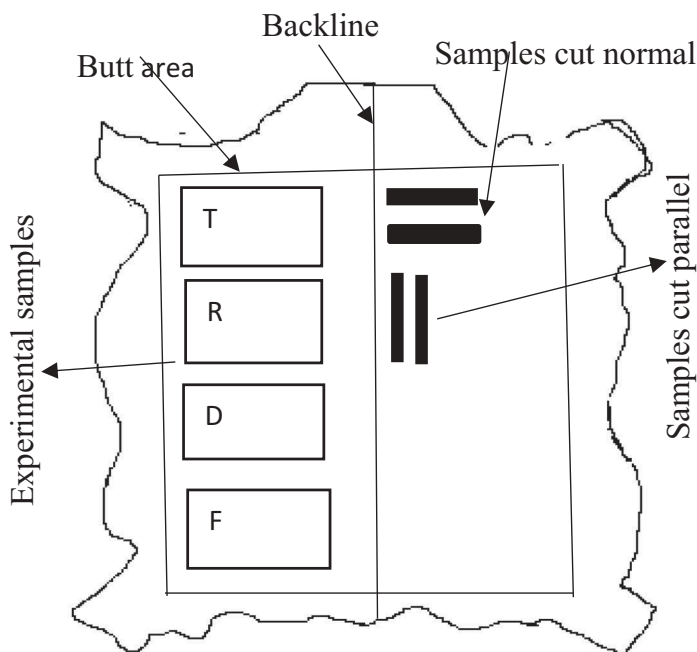
Figure 1. Representation of leather tanning and sample location.

The remaining three quarters proceeded to the retanning stage using chromium Sulphate in a drum. Before this stage, the wet blue was wetted in water, weighed, basified using sodium bicarbonate and then neutralised using ammonium bicarbonate. Antimould of 1% and 2% of the sodium formate was also added during this neutralisation to adjust the pH to 6.5. Retannage was carried out using 150% water at 45°C and 6% retannages agent (chromium sulphate) in a drum running moderately slow for 45 min. After penetration check, 1.5% formic was added to fix the crust. The crust was then drained, washed and toggled overnight prior to dyeing. A third of the crust was cut out within the butt area as a retanned sample (R). To prepare the crust for dyeing, the remaining piece was basified using ammonium bicarbonate to adjust the pH to 6.5. Dyeing involved 100% water at 50°C and 2% of black dye added through the axle as the drum runs. The crust was then fixed using formic acid before it was drained, washed and toggled overnight. Half of the crust was cut out within the butt area as a dyed sample (D). The remaining crust was fatliquored. One hundred per cent of water at 50°C and 2% of fat liquor were run in a drum for 45 min. The fatliquored crust was then fixed in 1.5% of formic acid to lower the pH to 3.5. The crust was then drained and washed in 200% water, and toggled overnight. The sample is labelled as a fatliquored (F).

2.2. EDXRF instrumentation and analysis

Figure 2 shows a typical schematic EDXRF (RIGAKU NEX CG) spectrometer operated at applied power and voltage of 50 W and 50 kV, respectively, in the X-ray tube and current of 2 mA.
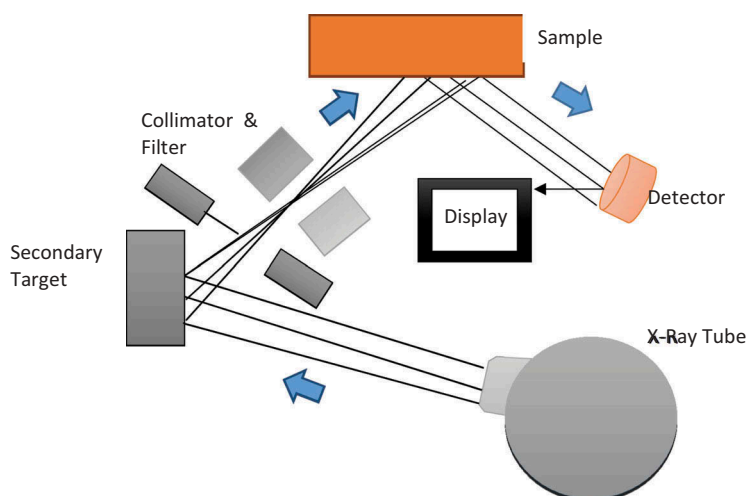
Figure 2. Schematic illustration of EDXRF-Rigaku NEX CG secondary excitation.

The spectral data measurements were obtained in air at dead time less than 25% with all characteristic lines of the particular elements automatically assigned by the Fundamental Parameter software. The secondary target was selected automatically depending on the components contained in a sample and elements were analysed with the conditions shown in Table 1.

The versatility of this spectrometer is due to the close-coupled Cartesian Geometry (CG) optical kernel that increases the signal-to-noise ratio. The EDXRF has 3D optics whereby the primary polychromatic X-rays from the tube irradiate a polarising target (secondary target) placed along the first axis [30]. Polarising targets scatter the primary rays at 90° which form the second axis to the sample. The scattered rays then reach the semiconductor detector placed along the third axis [31] Scattering eliminates the primary beam thereby reducing the spectral background. Polarised excitation (secondary targets) enhances optimisation of the excitation source for particular analytes to be analysed and improves the limits of detection. Circular leather samples of 32 mm diameter were cut from the leather crusts and placed in polypropylene sample cups. Measurements were carried out in vacuum and analysis was controlled by a PC data acquisition system. The spectral data were recorded in the range 0–40 keV, with a spectral resolution of 150 eV for K_α. The quantification of samples' concentration was achieved using the advanced FP (fundamental Parameter) software equipped with a superior algorithm called Rigaku profile fitting-spectra Quant X (RPF-SQX) [32,33]. The fundamental parameter method is founded on a theoretical relation between the measured x-ray intensities and the

Table 1. Excitation conditions of measurement.

Secondary target	Tube voltage (kV)	Tube current (mA)	Measurement time (s)
Si	50	Automatic	100
Al	50	Automatic	200
Mo	50	Automatic	100
Cu	50	Automatic	100
RX9	25	Automatic	100

corresponding concentrations of elements in the material. The quantification is a factor of interactions and absorption between the photons and atoms, the thickness of the atomic layer and elemental composition [33]. The algorithm allows the standardless analysis based upon the theoretical equations, the fundamental database and precise modelling of the silicon detector which is more efficient than linear calibration for the quantification of the study elements [34].

3. Results and discussion

The average of 15 spectral intensities of elements in tanned, retanned, dyed and fatliquored crusts for the five excitation conditions (secondary targets) are shown in Figures 3–6.

The predominance of Cr, S, Na and Cl dwarfed the intensities of the other minor elements in leather crusts as shown in Figures 3–6. The Cu secondary target showed excellent excitation efficiency for most of the elements detected such as K, Ca, V, Cr, Mn, Cu and Zn. RX9 secondary target exhibited excellent excitation efficiency for S, Na and Cl whereas Mo target only showed efficiency to detect Zr and Mo. The Al and Si secondary targets detected Al and Si, respectively. Although a combination of the five secondary targets gives a wide range of detection of different elements, a combination of RX9 and Cu is sufficient to efficiently detect key elements in post-tanned crusts.

The average elemental concentrations from 15 samples in tanned, retanned, dyed and fatliquored leather are summarised in Table 2.

Abundance of the elements in all the post-tanned leather crusts was in the order Cr > S > Na > Cl > Al > Si > Ca > V > K > P > Zr > Zn > Fe > Mn > As > Ti > Cu > Pb > Ni > Ga > Br > Hg. The concentrations of total Chromium ranged from 63967 to 80100 mg/kg, total sulphur 23967 to 49967 mg/kg, total sodium 23967 to 27567 mg/kg while total chlorides from 1667 to 9347 mg/kg. These values are by far higher than the minimum recommended
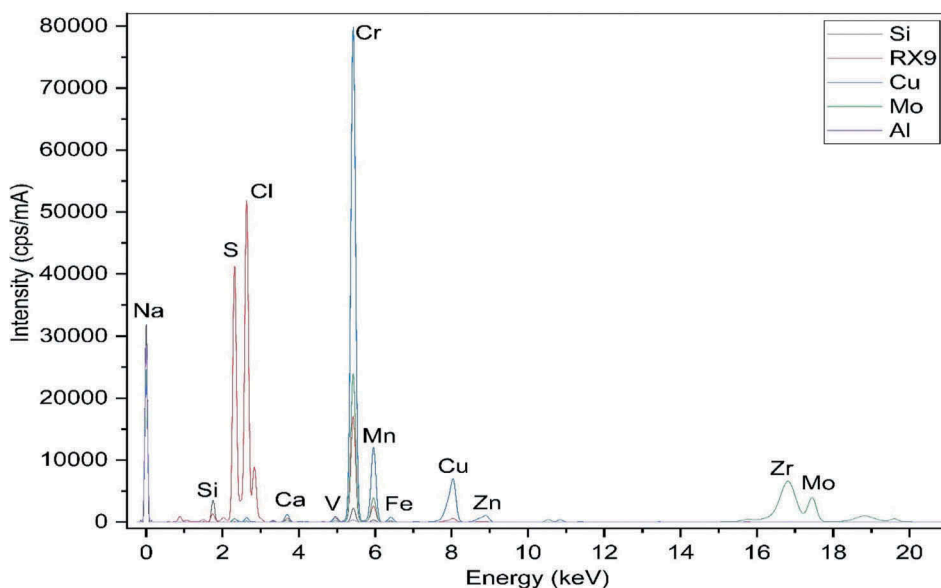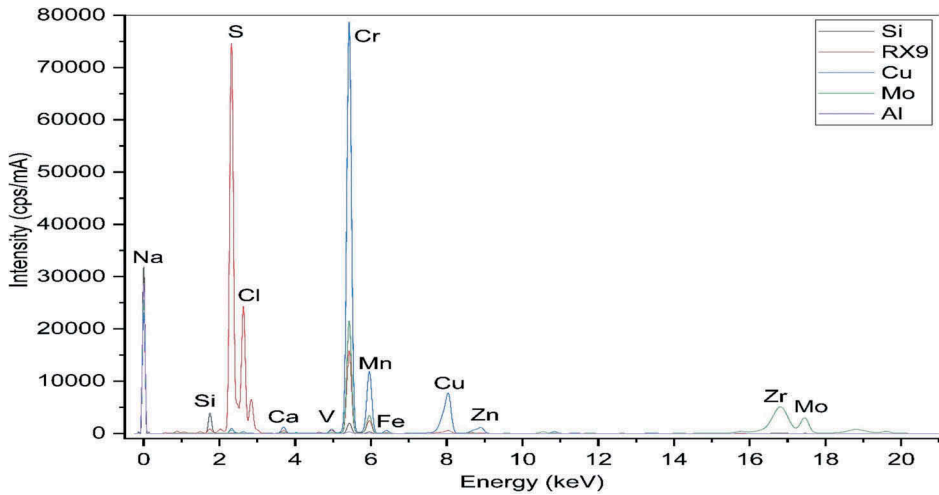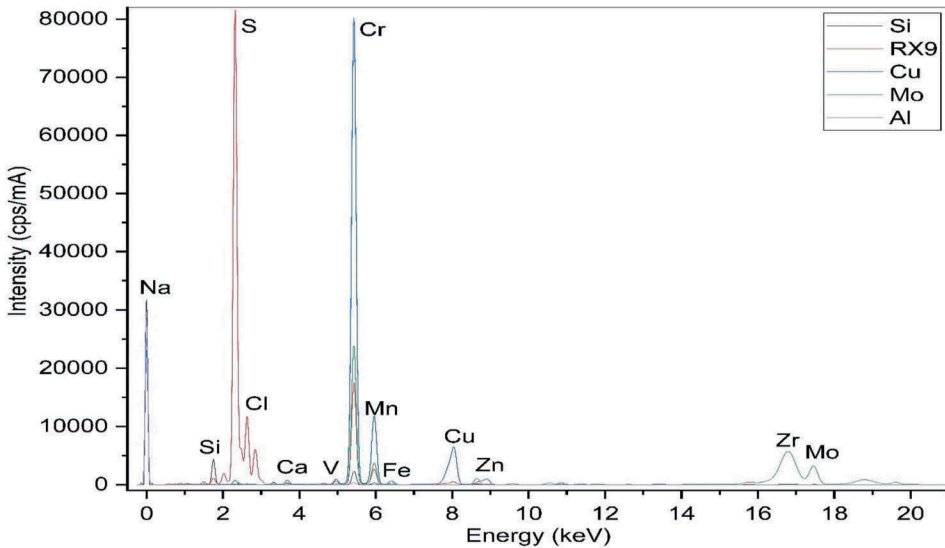

Figure 3. Average spectra of elements in tanned crust by five secondary targets.
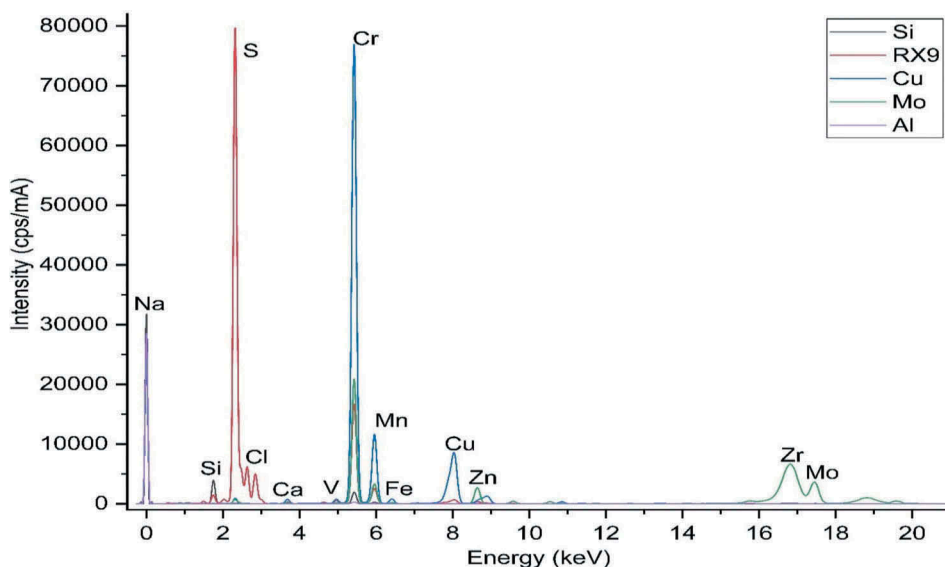
Figure 4. Average spectra of elements in retanned crust by five secondary targets.

Figure 5. Average spectra of elements in dyed crust by five secondary targets.

values in BS EN 71-3 and SG criteria list for leachable chromium of 60 ppm and 3 mg/kg, respectively. These concentrations are higher than the values reported in other related studies due to differences arising from the processing recipes and the techniques of measurement. Total chromium, for instance, consists of the chromium that forms the polynuclear crosslinks between carboxyl groups of the collagen molecules and the chromium that remains suspended between fibres [35]. During leaching, only the suspended chromium gets leached in the acid solutions [36]. The values reported in this study comprise both the suspended and the complex bridges formed unlike in ICP OES whose values represents the leachable elements only. Furthermore, in this study,

Figure 6. Average spectra of elements in fatliquored crust by five secondary targets.

Table 2. Average elemental concentrations in tanned, retanned, dyed and fatliquored leathers.

Element	Elemental concentration by means ± standard deviation (mg/kg) (N = 60)			
	Tanned	Retanned	Dyed	Fatliquored
Cr	69200 ± 129.7	80100 ± 136.67	75167 ± 151.3	63967 ± 118.7
Hg	3.53 ± 1.12	4.33 ± 1.21	<3.28*	3.36 ± 1.1
Pb	12.6 ± 1.4	14.4 ± 1.52	13.1 ± 1.51	17.5 ± 1.6
As	101 ± 2.04	94.1 ± 2.13	95.6 ± 2.16	82.2 ± 1.88
V	1046 ± 16.4	1417 ± 17.47	1048 ± 20.4	832.3 ± 14.34
Mn	163 ± 45.7	<156.3*	<149*	<133*
Fe	439.3 ± 12.4	386.7 ± 12.07	364.7 ± 12.1	390.7 ± 11.23
Ni	7.49 ± 1.55	9.67 ± 1.8	9.19 ± 1.71	8.94 ± 1.7
Cu	15.5 ± 1.66	17.3 ± 1.91	19.5 ± 1.9	16.4 ± 1.75
Zn	19.43 ± 1.46	760.7 ± 2.76	81.53 ± 8.63	1370 ± 10.8
P	319 ± 10.82	1633 ± 12.6	397 ± 21.47	292 ± 9.8
K	661.3 ± 34.1	2717 ± 35.57	561.7 ± 66.3	414.3 ± 29
Ca	3257 ± 65.03	1717 ± 67.07	2907 ± 60.67	981 ± 48.2
S	23967 ± 53.2	49967 ± 78.97	48167 ± 79	42500 ± 65.97
Na	23967 ± 3783.3	15633 ± 4070	27567 ± 2943.3	11667 ± 2980
Ti	44.3 ± 6.57	57.83 ± 6.74	41.03 ± 6.9	45.9 ± 6.01
Zr	598 ± 17.87	623 ± 19.77	646 ± 19.4	604 ± 17.87
Ga	5.78 ± 0.86	9.41 ± 0.91	5.93 ± 1.1	9.34 ± 1.05
Al	3257 ± 106	4123 ± 117	3533 ± 118.7	2550 ± 88.37
Si	3490 ± 52.77	2633 ± 52.53	3097 ± 46.73	2837 ± 44.13
Cl	17267 ± 32.8	4267 ± 26.47	9347 ± 18.17	1667 ± 10.04
Br	6.38 ± 0.56	2.92 ± 0.51	3.73 ± 0.55	<1.2*

*< Below detection level of the equipment.

chromium sulphate was used during both tanning and retanning processes, a fact that contributes to a high content of suspended salts and hence high concentration values. Studies by Zhao et al. [37] reported the concentrations of Cr in the leathers to be 34,246 mg/kg using MIP OES technique while 23,407 mg/kg using WDXRF by Neiva et al. [28]. The concentrations for Cr in tannery effluents as determined by Aslan [25]

using ICP OES ranged between 28000 and 44000 mg/kg. The results reported in this study for Br, Zn, Ni, Cu and Fe agree with results reported by Kapel and Speak [38], Carneiro et al. [39] and Okoh et al. [14], although the concentrations for Arsenic (As) were slightly higher. SG criteria list gives the limits for Cu and Ni as 60 and 1 mg/kg, respectively. The value for Cu reported here is less than the limit while the value for Ni is slightly higher than the recommended minimum. The limit values for As in BS EN 71-3 and SG criteria list are 25 ppm and 0.2 mg/kg, respectively. The higher concentrations of As may be attributed to the impurities in the chemicals and on the instruments used and acaricides and other pesticides used on the animal for tick management [14,35,40]. These studies used ICP-OES, INAA and AAS techniques to determine the concentrations, which have different limits of determination and quantification. The higher concentrations of chromium, sulphur, sodium and chlorine can be attributed to their excessive use during preservation (industrial salt), dehairing (sodium sulphide), deliming (sodium metabisulphite), pickling (sodium chloride and sulphuric acid), tanning and retanning (chromium Sulphate), basification and neutralisation using sodium formate and sodium bicarbonate [41,42]. The values for mercury and lead reported in this study are way below the limit values of 60 and 90 ppm allowed by BS EN 71-3, respectively. The sources of mercury can be traced back to the fungicides and biocides used in the processing while lead can be attributed to the accumulation in animal hides from lead sources in the natural surroundings and after slaughtering such as lead chromate-based pigments [40].

Principal component analysis (PCA) was employed to identify the pattern in the elemental concentration during post-tanning operations in order to determine the effects of post-tanning operations on the elemental compositions of the resulting leather using spectral raw data. Figure 7 shows the score plot for post-tanned crusts.

The first two principal components explained 97.9% of variance of the entire data. The remaining 7% variation could be attributed to the presence of outliers. From the plot, all
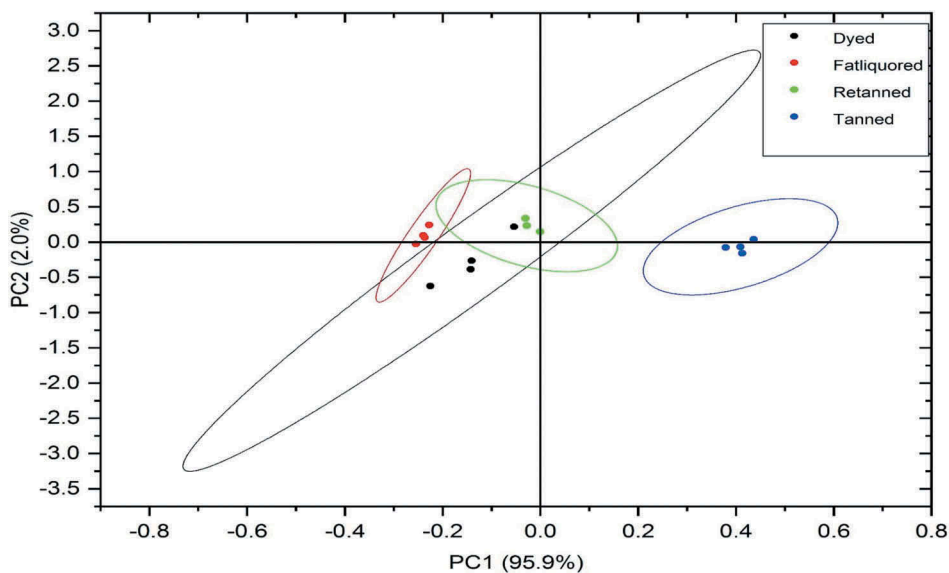

Figure 7. Score plots for all post-tanned leather crusts.

the four processes have an effect on both elemental composition and concentration as evidenced by classification of scores for each process. The first component (PC 1), which accounts for 95.9% of the variation in data, separates fatliquored and tanned crust composition while PC 2, which accounts for 2.0% of the variations, separates the dyed from the retanned crusts. The tanned samples show high positive scores while fatliquored samples show high negative scores along component 1. Similarly, retanned samples showed positive scores while dyed samples showed negative scores. To determine the elements that account for these differences, examination of variable loadings was done on the first two components as shown in Figure 8.

The valuable tracers for the classification over various stages of processing are Cr, S, Cl, P, V, K, Mn and Zn. To determine the possible provenance and hence their pathway during post-tanning processes, comparisons were made at each progressive stage. Comparison of the score plots of two successive processes was done. The elements that distinguish chemical elements of tanned from retanned crusts are S, Cu and chlorine as shown in Figure 9.

Retanning introduces more sulphur and copper into the leather fibres. This is attributed to the Sulphate salts used in retanning (second chrome tanning) process. However, the levels of chloride salts decrease as retanning progresses. The main source of Cl is the salt used during preservation and pickling. These salts are meant to inhibit any bacterial growth but their chemical reaction with the collagen is minimal and hence the majority of the salts are physically suspended in the fibres and get displaced easily as retanning progresses [43]. This explains why Cl is lower at retanning than at tanning. Figure 10 shows the loading plot of retanned and dyed crusts.

The first two components accounted for 98.6% of the variations in the chemical elements of the two crusts. Therefore, the two components were sufficient to explain the variations and it can be seen that most of the scores for dyed crust are negative while positive for retanned crusts. The elements responsible for the loadings in PC 1 are
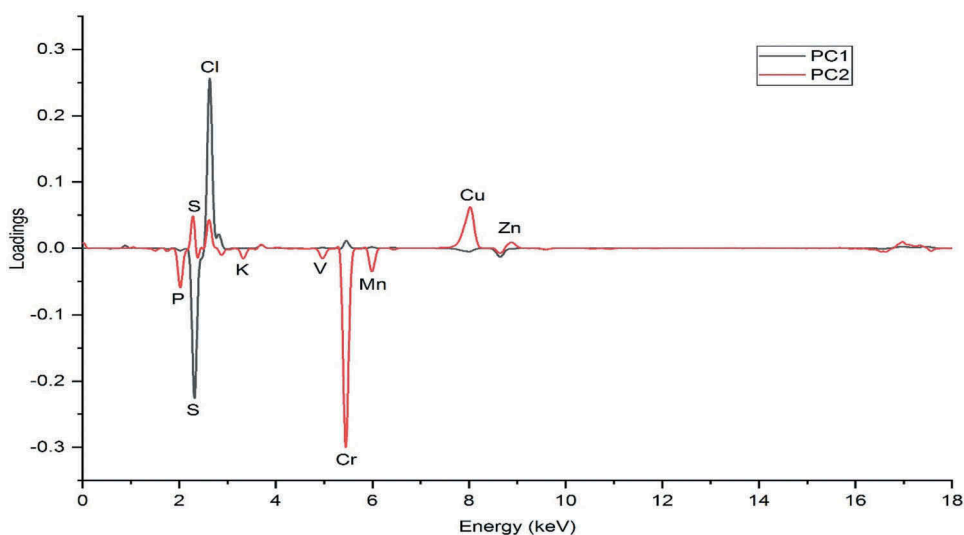

Figure 8. PCA loadings plot showing the trace elements responsible for the PCA clusters.
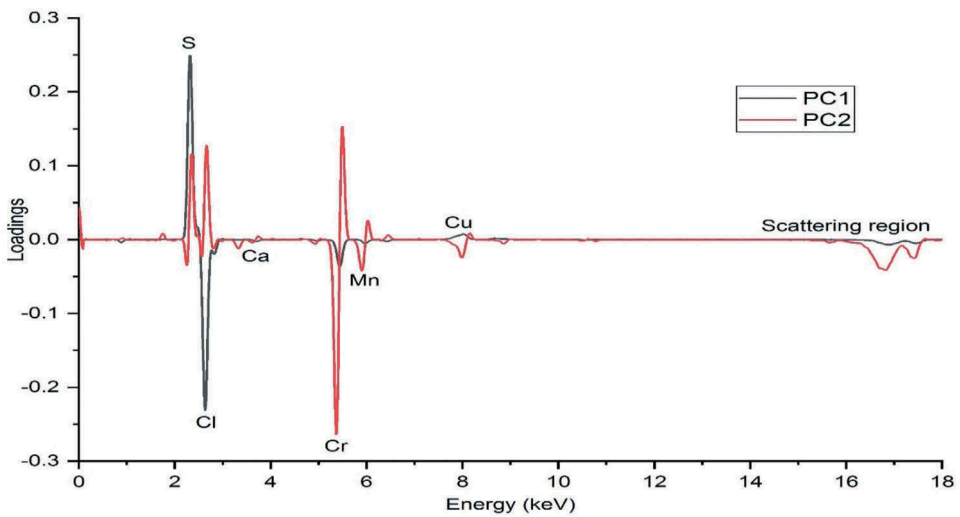
Figure 9. PCA loadings of elements for clusters of tanned and retanned crust.
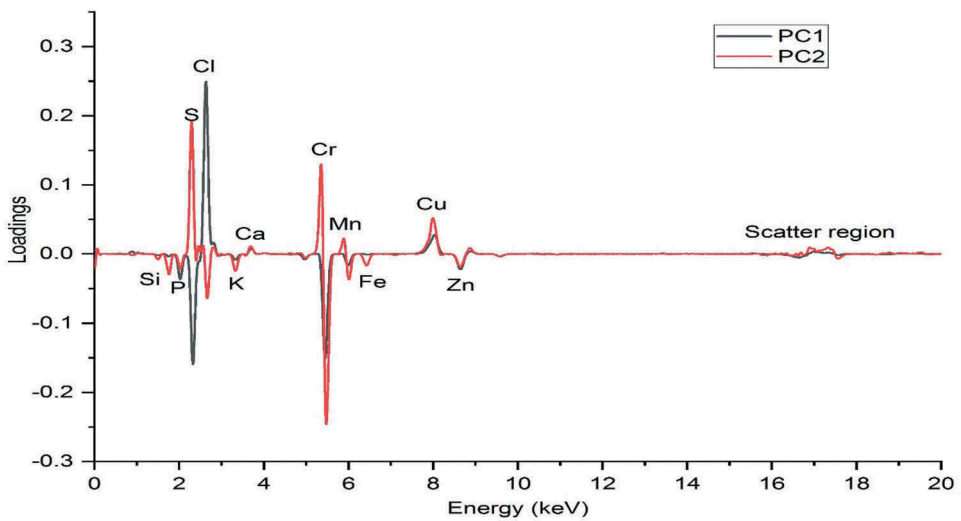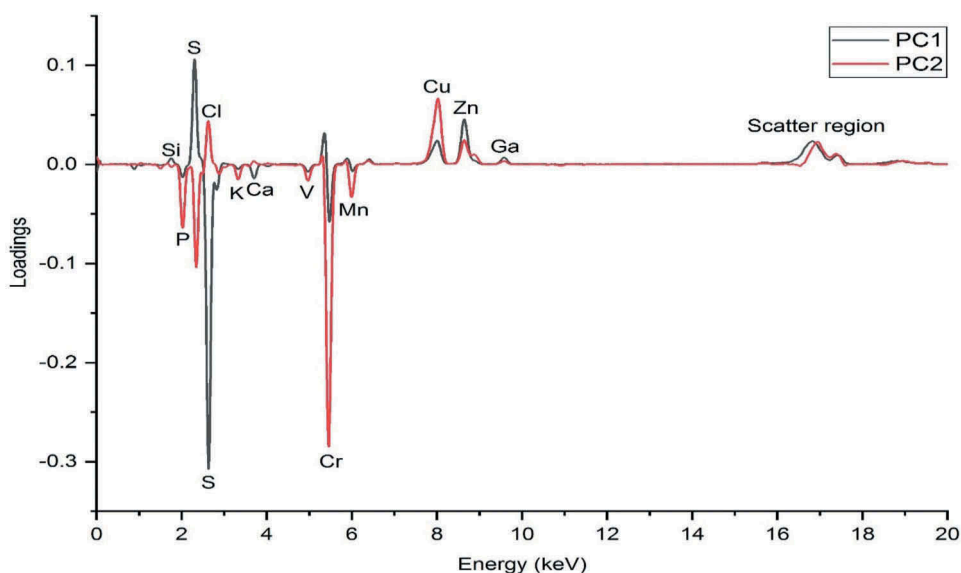

Figure 10. PCA loadings of elements for clusters of retanned and dyed crust.

Cl, P, K, S, Cr and Cu. Dyeing process raises the levels of P, S, K, Mn and Zn and lowers the levels of Cl and Cu. Dolgin et al. [44] have attributed the presence of Mn in parchment to be calcites. Similarly, Cl and Cu get displaced as processing progresses. The source of P, S, K, Zn and Mn may be present in dyes used due to colourants and pigments in the dye [27,45,46]. Figure 11 shows the loading plot of dyed and fatliquored crusts.

PC 1 and PC 2 explain 97.2% of the variation in the chemical elements in the dyed and fatliquored crusts. The elements responsible for the variations are P, S, Ca, V, Cu, Zn and Ga. Fatliquoring process increases the concentration levels of S, Si, Ga, Cu and Zn. The

Figure 11. PCA loadings of elements for clusters of dyed and fatliquored crusts.

fatliquors used in this study were sulphited and hence this explains the increase in sulphur elements.

4. Conclusion

The abundance of the elements in all the leather crusts was in the order $Cr > S > Na > Cl > Al > Si > Ca > V > K > P > Zr > Zn > Fe > Mn > As > Ti > Cu > Pb > Ni > Ga > Br > Hg$. The concentration levels for the majority of the elements in all the crusts were higher than the recommended minimum for many applications such as children toys (As-25 mg/kg and total Cr-60 mg/kg). Combination of EDXRF and principal component analysis has shown to be vital in the leather industry to monitor chemical concentration. This combination will be useful for human health-based quality control system along the leather tanning processes. This will be useful in determining and evaluating tanning recipes based on the end use of the final leather especially the toxic elements that in leather that have shown to be carcinogenic. A combination of Cu and RX9 secondary targets exhibited sufficient and excellent excitation efficiency for the majority of the elements detected in leather crusts. The valuable tracers for classification in the post-tanning operations are Cr, S, Cl, P, V, K, Mn and Zn. Retanning increases sulphur and copper elements in the crusts while decreasing the levels of Cl. Dyeing and fatliquoring processes raise the concentrations of sulphur in leather crusts while decreasing Cl. The study will inform the vetting of different recipes and regimes of tanning.

Disclosure statement

Funding

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