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RESEARCH ARTICLE

Analysis of Chrome Tanned Leather Shavings Using Neutron Activation Analysis

S. S. ACHI[1*], D. J. ADEYEMO[2], C. MAJU[3] and J. TAGANG[3]

[1]Chemistry Department, Bingham University, Karu, Nasarawa State, Nigeria
[2]Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria
[3]Federal College of Chemical and Leather Technology, Zaria, Nigeria
dr_achi03@yahoo.co.uk

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Abstract: Chrome tanned leather shavings collected from the federal college of chemical and leather technology (CHELTECH) Zaria, Nigeria's tannery were analyzed using centre for energy research and training (CERT), Zaria Nigeria's miniature neutron source reactor (MNSR). The main aim of this work was to determine the concentration of chromium and other constituents of the shavings. Chromium is known for its human toxicity which includes skin irritation, lung cancer, as well as Kidney, liver and gastric damages. The disposal of this waste without treatment will constitute a serious impact on the environment. The result obtained indicates that Chromium is as much as 1%. The analyzed concentrations of As, Ba, Br, Co, Fe, La, Na, Sb, Sc, Sm and Zn in the sample are also presented. The results obtained were validated with the data obtained from the analysis of certified reference materials, IAEA-336 (Lichen) and IAEA 359 (Cabbage).

Keywords: Chrome tanned leather, Neutron activation analysis, Radionuclides

Introduction

Leather industry is one of the oldest cottage industries in Nigeria. Although tanning has been in existence for a long time, the problem of environmental pollution received serious consideration only in recent years. The pollutants from large tanneries have caused considerable damage to water courses, affecting drinking water supply, irrigation and aquatic life. It is realized that the untreated wastewater when allowed to stagnate, gives rise to odour nuisance, unsightly appearance creating ground and surface water pollution. Against this background, it is evident that pollution control is just unavoidable for the tanning industry to keep its environment clean and pollution free[1].

When tanners shave the bottom sides of chrome-tanned hides to give them a uniform thickness, so-called chrome shavings end up as waste that must be hauled to landfills at a price. Wastes can be utilized to generate useful by-products.

The solid wastes coming from leather tanning with trivalent chrome salts (scraps leather and shavings) need a special attention due to the amount produced. One tonne of wet hide yields only 200 kg of leather but over 600 kg of solid waste or by-product[2]. It has been reported that about 600,000 of solid wastes each year worldwide are generated by the leather industry and approximately 40-50% of the hides are lose shavings and trimmings[2]. Chrome shavings constitute about 75% of the solid waste containing chromium in the tanning process.

Chromium exists in environment both as trivalent [Cr(III)] and hexavalent [Cr(VI)] forms of which the hexavalent form is 500 times more toxic than the trivalent one[3]. Human toxicity of Cr(VI) includes skin irritation to lung cancer, as well as kidney, liver and gastric damage[3].

Since chromium is known for its toxicity, the disposal of chrome shavings has been identified as a serious problem from the environmental point of view. Sastry *et al*[4] developed two processes to offer an alternative and better solution for the disposal of chrome shavings. The first process is preparation of parchment-like membrane and the second process is related to development of leather-like material. The utilization of the chrome shavings in preparation of those two products not only reduces the environmental pollution but at the same time value added products can also be obtained.

Neutron activation analysis is a technique which, makes it possible to determine large number of elements in different types of matrices[5]. The Nigerian Research Reactor-1(NIRR-1) was used for the analysis. The NIRR-1 has a tank in pool structural configuration and a nominal thermal power rating of 31 (kW) with a built in clean cold core excess reactivity of 3.77 mk measured during the on-site zero power and criticality experiments. Under these conditions the reactor can operate with the same fuel loading for over ten (10) years with a burn up of <1%. Neutron flux parameter of MNSRs are known to be stable, thus permitting the use of semi absolute Neutron Activation Analysis (NAA)[5-9]. NAA in its instrumental form, has some unique features which makes it attractive to use for routing analysis.

Experimental

Chrome shaving samples collected from the CHELTECH tannery to be analyzed were dried then ground into a powdered form of 125 µm grain size. 250 mg-300 mg of the powdered samples were weighed.

NIRR-1 which is a low-power nuclear reactor with highly enriched uranium as fuel, light water as moderator and beryllium as reflector was used. The reactor's associated facility for radioactivity measurements are a gamma ray data acquisition system. It consists of a horizontal dip-stick High Purity Germanium (HPGs) detector with a relative efficiency of 10% at 1332.5 keV gamma ray line, MAESTRO emulation software compatible with the ADCAM® Multi-channel analyzer (MCA) card, associated electronic modules and a personal computer. For data processing gamma ray spectrum analysis, software WINSPAN 2004[10] in addition to NAA calculations, perform peak analysis, remote control of MCA and other auxiliary functions such as efficiency calibration and nuclear data generation.

For irradiation, two schemes (long and short) were adopted based on the half-life of the product radionuclide. For elements leading to short-lived activation products the samples are each packed and sealed in 7 cm^3 rabbit capsules and sent for irradiation in turn in an outer irradiation channel B_4 where the neutron spectrum is "soft", the choice of the outer irradiation channel is to eliminate corrections, notably Mg in the presence of P. This is due to the proximity of the inner channels of MNSRs to the core leading to relative higher ratio of fast-to-thermal neutron[9].

For elements leading to long-lived activation products, samples wrapped in polyethylene films were then irradiated for 6 h in any of the small inner irradiation channels (*i.e.* A_1 , B_1, B_2 and B_3) to take advantage of the maximum value of thermal neutron flux in the inner channels.

Radioactivity measurements of induced radionuclides were performed by the PC-based gamma ray spectrometry set up. Following the short irradiation regime the first round of counting was performed for 10 min (*i.e.* S1) after a waiting time of 2-15 min. Samples were placed on a Plexi-glass sample holder designated “H2” which corresponds to source-detector geometry of 5 cm. The second round of counting was also carried out for 10 min. following the short irradiation regime (*i.e.* S2) after a waiting period of 3-4 h. Samples were counted on a Plexi-glass holder designated as “H1” corresponding to a source-detector geometry of 1 cm. The neutron flux setting for the short irradiation of the sample was raised to $5x10^{11}$ n/cm/s sensitivities for analysis using procedures S1 and S2.

In the case of the long irradiation scheme, the first round of counting was carried out for 30 min following the long irradiation (*i.e.* L1) using the holder “H 1” after a waiting period counting was performed for 60 min (*i.e.* L2) after cooling time of 10-15 days. The samples were counted using the Plexi-glass holder “H1”. The Choice of cooling time and sample detector geometry was such that detectors’ dead time is controlled to be less than 10%. For the biological material the certified reference material IAEA-359 (Cabbage) and IAEA-336 (Lichen) were chosen.

Results and Discussion

The irradiation and counting schemes together with the WINSPAN multi-element gamma-ray analysis software have been validated using the standard reference materials. Results printed in Table 1 give the routine irradiation and measuring regimes developed for NIRR-1 facilities. Table 2 gives comparison of certified values with our results in ppm or as indicated in %for certified biological reference material, IAEA-336 (Lichen) and IAEA-359 (Cabbage). Table 3 gives nuclear data and limits of detection for the elements of interest using adopted experimental conditions. Table 4 gives the analytical results of INAA of chrome shavings.

Table 1. Routine irradiation and measuring regimes developed for NIRR-1 facilities

Neutron flux/irradiation channel	Procedure	T_{irr}	T_d	T_c	Activation products
$1x10^{11}$n /cm^2 s /outer irradiation channels (B4, A2)	S1	2 min	2-15 min	10 min	^{28}Al, ^{27}Mg, ^{38}C1, ^{49}Ca, ^{66}Cu,^{51}Ti, ^{52}V, ^{116m}In
	S2	2 min	3-4h	10 min	^{24}Na, ^{42}K, ^{165}Dy, ^{56}Mn, ^{152m}Eu
$5x10^{11}$ n /cm^2 s /inner irradiation channels (B1,B2,B3, L2 and A1)	L1	6 h	4-5d	30 min	^{239}Np (U), ^{72}Ga, ^{122}Sb
	L2	6 h	10-15d	60 min	^{46}Sc, ^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{152}Eu, ^{177}Lu, ^{131}Ba, ^{86}Rb, ^{182}Tb, ^{175}Yb, ^{233}Pa (Th), ^{65}Zn, ^{59}Fe’ ^{181}Hf

Table 2. Comparison of certified values with our results in ppm or as indicated in % for the certified reference materials, IAEA-336 (Lichen) and IAEA 359 (Cabbage)

	IAEA-336(Lichen)	(CV)	IAEA-339 (Cabbage)	
Element	This work (TW)		This Work (TW)	(CV)
Al	709±35	570-790	175± 13	0.096-0.104
As	BDL	0.55-0.71	BDL	10.5-11.5
Ba	11.0± 1.3	5.3-7.5	BDL	-
Br	BDL	-	8.0±3.0	1.8-1.9
Ca (%)	BDL	1.11-1.45	1.97+ 0.12	-
Ce	BDL	0.24-0.34	BDL	-
Co	BDL	0.89-1.23	BDL	1.24-1.36
Cr	BDL	0.097-0.123	BDL	-
Cs	BDL	144	BDL	78.6
Cu	BDL	0.019-0.027	BDL	-
Eu	BDL	0.038-0.048	BDL	0.014-0.15
Fe, %	BDL	0.16-0.21	BDL	-
K, %	0.66±0.04	0.56-0.76	3.3 ± 0.4	-0.21-0.22
La	BDL	0.004-0.009	0.27 ± 0.05	31.3-32.5
Lu	BDL	-	BDL	567-601
La	61± 2	56-70	BDL	-
Mg, %	317±16	280-360	29.4 ± 0.8	-
Mn	BDL	1.54-1.98	676 ± 30	-
Na	BDL	0.063-0.083	BDL	-
Rb	0.16± 0.03	0.15-0.17	BDL	-
SB	BDL	0.092-0.12	BDL	-
Sc	BDL	0.012-0.016	BDL	-
Sm	BDL	0.12-0.16	BDL	-
Tb	BDL	1.25-1.69	BDL	-
Th	BDL	0.025-0.049	BDL	-
V	BDL		BDL	-
Yb	BDL		BDL	-
Zn	BDL	27.0-33.8	BDL	-

BDL- below detection limit

Table 3. Nuclear data and limits of detection for the elements of interest using adopted experimental conditions

Target isotope	Product isotope by (n, γ) reaction	Half-life	Gamma-energy KeV	LOD, ppm
^{23}Na	^{24}Na	14.96 h	1368.60	40 (L1)
^{26}Mg	^{27}Mg	9.46 min	1014.4	7250 (S1)
^{27}Al	^{28}Al	2.24 min	1778.99	17 (S1)
^{37} Cl	^{38}Cl	37.24	1624.7	2900 (S1)
^{41}K	^{42}K	12.36 h	1524.58	2400 (S2)
^{45}Sc	^{46}Sc	83.81d	889.28	0.2 (L2)
^{48}Ca	^{49}Ca	8.72 min	3084.54	6600 (S1)
^{50}Ti	^{51}Ti	5.76 min	329.08	2500 (S1)

Contd…

^{50}Cr	^{51}Cr	27.7d	320.98	23 (L2)
^{51}V	^{52}V	3.75 min	1434.08	15 (S1)
^{55}Mn	^{56}Mn	2.58 h	846.76	0.9 (S2)
^{58}Fe	^{59}Fe	44.5d	1099.25	829 (L2)
^{59}Co	^{60}Co	5.27y	1173.2	3.0 (L2)
^{65}Cu	^{66}Cu	5.10 min	1039.2	172 (S1)
^{64}Zn	^{65}Zn	243.9d	1115.55	120 (L2)
^{71}Ga	^{72}Ga	14.1 h	834.1	1.0 (L1)
^{75}As	^{76}As	26.32 h	559.10	1.2 (L1)
^{81}Br	^{82}Br	35.3 h	776.5	3.0 (L1)
^{85}Rb	^{86}Rb	18.8d	1076.6	3.0 (L2)
^{115}In	^{116m}In	54.15 min	1097.3	0.5 (S1)
^{121}Sb	^{122}Sb	64.8 h	564.24	0.5 (L1)
^{133}Cs	^{134}Cs	2.06y	795.85	1.7 (L2)
^{130}Ba	^{131}Ba	11.8d	496.3	264 (L2)
^{139}La	^{140}La	40.3 h	1596.21	0.2 (L1)
^{140}Ce	^{141}Ce	32.5d	145.44	14 (L2)
^{151}Eu	^{152}Eu	13.3y	1408.5	0.6 (L2)
^{152}Sm	^{153}Sm	46.27 h	103.18	0.1 (L1)
^{159}Tb	^{160}Tb	72.3d	879.38	1.1 (L2)
^{164}Dy	^{165}Dy	2.33 h	94.70	0.7 (S2)
^{174}Yb	^{175}Yb	4.19d	396.33	0.9 (L1)
^{176}Lu	^{177}Lu	6.71d	208.36	0.1 (L2)
^{180}Hf	^{181}Hf	42.4d	482.2	1.1 (L2)
^{181}Ta	^{182}Ta	115d	1221.4	1.0 (L2)
^{197}Au	^{198}Au	2.7d	411.8	0.02 (L1)
^{232}Th	^{233}Pa	27.00d	312.01	1.2 (L2)
^{238}U	^{239}Np	2.36d	277.60	1.5 (L1)

S1, S2, L1 and L2 represent Irradiation and counting schemes adopted for the respective element

The results in Table 4 show that chrome shavings are characterized by both benign and toxic substances. The elements of serious concern from the results obtained are the heavy metals. The data given in Table 4 shows that chromium contributes up to 1.0±0.03% of the quantum of the toxic substances in the chrome shavings samples analyzed. This shows that chrome shavings have high pollution load in excess of legal requirements for discharge into public refuse. The high pollution load observed is characteristic of tannery wastes[11].

Turning to the question of clean production in regards to the results of this work (see Table 4), it is clear that leather production in the developing world generates waste that are characterized by heavy metals and other types of toxic substances. When compared with the Scottish Leather Group 2008 Environmental Report and Adidas 2009 Environmental Report on the use and disposal of leather and leather products waste, we find that the western world is well along the path towards cleaner leather making and waste management. This can be attributed to the fact that majority of the tanning industries in the developed world comply to the EU system for Registration, Evaluation and Authorization of Chemicals (REACH), the UK Landfill Allowances and Trading Scheme Regulations (LATS) and the US Environmental Protection Act 1990. The priorities in the developing world are different but rivers that will support life, agricultural land that will not grow plants, wells where the water has become non-potable, have become a powerful incentive to clean up the act.

Table 4. Determined Elements and Concentrations of Chrome Shavings using NIRR-1

Elements	Product isotope by (n, γ) reaction	Half-life	Gamma-energy KeV	Concentrations
Al	^{28}Al	2.24 min	1778.99	BDL
As	^{76}As	26.32 h	559.10	2.1±0.3 ppm
Ba	^{131}Ba	11.8d	496.3	13.2±3.3 ppm
Br	^{82}Br	35.3 h	776.5	10.4±0.5 ppm
Ca	^{49}Ca	8.72 min	3084.54	BDL
Co	^{60}Co	5.27y	1173.2	1.18±0.13 ppm
Cr	^{51}Cr	27.7d	320.98	1.0±0.03%
Cs	^{134}Cs	2.06y	795.85	BDL
Dy	^{165}Dy	2.33 h	94.70	BDL
Eu	^{152}Eu	13.3y	1408.5	BDL
Fe	^{59}Fe	44.5d	1099.25	1.84±0.04%
Hf	^{181}Hf	42.4d	482.2	BDL
K	^{42}K	12.36 h	1524.58	BDL
La	^{140}La	40.3 h	1596.21	1.3±0.1 ppm
Lu	^{177}Lu	6.71d	208.36	BDL
Mg	^{27}Mg	9.46 min	1014.4	BDL
Mn	^{56}Mn	2.58 h	846.76	BDL
Na	^{24}Na	14.96 h	1368.60	3.3±0.1 ppm
Rb	^{86}Rb	18.8d	1076.6	BDL
Sb	^{122}Sb	64.8 h	564.24	1.0±0.1 ppm
Sc	^{46}Sc	83.81d	889.28	0.5±0.02 ppm
Sm	^{153}Sm	46.27 h	103.18	1.12±0.03ppm
Ta	^{182}Ta	115d	1221.4	BDL
Tb	^{160}Tb	72.3d	879.38	NA
Th	^{233}Pa	27.00d	312.01	BDL
Ti	^{51}Ti	5.76 min	329.08	BDL
U	^{239}Np	2.36d	277.60	BDL
V	^{52}V	3.75 min	1434.08	BDL
Yb	^{175}Yb	4.19d	396.33	BDL
Zn	^{65}Zn	243.9d	1115.55	441±13 ppm

BDL: Below Detection Limit, NA: Not Analysed

The results of this work are in agreement with a similar work conducted by Mu, C. *et al.*[12] on discharge of chromium-containing leather waste. We have found out that the concentration of the various elements (*c.f.* Tables 3 and 4) vary with their results data within relatively narrow ranges. In another related work it was reported that the concentration of chromium in chrome shavings varies from 1.8-4.0% as chrome (on dry solid weight basis)[13] which is comparable with the percentage of chrome detected in our analysis.

On the other hand, the data provided by Aslan[14] showed a significant difference in the values of the concentration of the various elements detected in the present work. The concentration of the elements presented in Table 4 are higher than those published in Aslan'sdata. The results revealed that the principles for sustainable industrial practice set out in Agenda 21 of the 'Earth Submit' Rio Conference on waste management[15] have not fully been adopted by the leather industry, particularly in the developing countries.

On close examination of the results of this work *vis-a-vis* the Nigerian Environmental standards for discharge of waste containing chromium[16], we have found out that leather production in Nigeria generates waste that contain high concentration of hazardous substances. For example, the allowable minimum limit for disposal of chromium (Cr^{3+} and $Cr^{6+)}$ to sewers is 0.5 ppm and 0.1 ppm, respectively and our results show that Cr in the chrome shavings analyzed is 10,000 ppm. It is important to point out here that the chief danger posed to the well-being of humans and other living things by indiscriminate disposal of hazardous wastes such as chrome shavings, even if stored in a non-aqueous environment like a land fill or buried underground in containers-lies in its potential to contaminate natural waters by migrating from its point of deposition by say, leaching[17].

Other elements found in the chrome shavings as given in Tables 3 and 4 (Mg, Ca, *etc.*) can be attributed to the use of the salts of these elements for the basification of chrome tanned leathers. And the presence of other elements like Ca, Na, *etc* can be linked to the use of alkali in the pre-tanning treatment of hides/ skins. Based on the results of the analysis and the classification of wastes type outlined by Rahimifard[18], chrome shavings can be categorized as 50% biodegradable waste.

Conclusion

The results have revealed the nature of chrome shavings generated from the tanning industry and have shown that the world environment is threatened by incessant pollution through disposal of leather wastes and other industrial wastes. In order to be able to save the environment from further degradation or increases in the accumulated amounts of hazardous waste in the future, some industrial operations should be designed in such a way that the "four Rs" (reduction, recycling, reuse and recovery) principle of waste management are employed in order to prevent any pollution from leaving a plant site.

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