Determination of Some Trace Elements in Leather

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Abstract

In 2009 twelve leather samples were collected from 4 different locations in the ancient city of Kano, Nigeria, for the analysis of its trace element composition. ***The*** *locations included a tannery, a leather crafts market, leather dump site and a local tanning market. These samples were analysed using Instrumental Neutron Activation Analysis (INAA) technique. The samples were sent into the inner site of the Nigerian Research Reactor (NIRR-1) and irradiated for 6 hours at a neutron flux of* $5x10^{11}$ $ncm^{-2}s^{-1}$*. The spectrum for each sample was evaluated and the following elements were determined in varying concentrations in some of the samples: As, Br, Co, Fe, Rb, Sb and Zn. Out of the determined elements, As and Sb are of toxicological concern. In two of the leather samples, As was determined as 4.6 ± 0.6 mg/kg for a sample from dump site and 3.5 ± 0.6 mg/kg for a sample from the local tanning market. However, both the As and Sb concentrations were below the set limit of 25mg/kg and 60mg/kg respectively by the EU.*

Keywords: Leather, Trace elements, Concentration, Neutron Activation Analysis

Introduction

Worldwide, there has been an increasing awareness of the effect of trace metals to human health. The high concentration may prove toxic, as also, depletion in the concentration of the essential trace elements may cause various metabolic instabilities due to enzyme dysfunction (Anath, 2005).

Trace elements are commonly cited as significant contaminants because of their general environmental ubiquity and ease of assimilation in the food chain. They are of unique concern because their environmental and toxicological impact is highly dependent on the different chemical forms in which they occur (Jerome and Milagros 1993).

Several metal ions such as sodium, potassium, magnesium and calcium are essential to sustain biological life. At least six additional metals, mainly transition metals are essential for optimal growth, development and reproduction i.e. manganese, iron, cobalt, copper, zinc and, molybdenum.

In addition to the metals essential for human, water and air may contain toxic metals like mercury, lead, cadmium, chromium, silver, selenium, antimony, aluminium, arsenic and barium. These metals can cause chronic or acute poisoning and should be eliminated as much as possible from the living environment (Anath, 2005).

Tanning or permanent preservation, is the process by which putrescible proteinous matter in hide or skin is made non-putrescible (Santappa *et. al*, 1982). The two major approaches to tanning are vegetable and chrome. Vegetable tanning uses aqueous infusions of polyphenolic materials of plant origin while chrome tanning uses basified salts of Cr (III). Chrome tanning in particular, has gained importance in leather processing during the last two decades (Chandrasekaran. *et. al*, 1999).

It is important to have adequate information about the composition of trace elements in leather, because some of the elements could prove toxic to man at certain concentrations.

A study to determine Cr in leather samples, by Okoh *et al*, (2012) using INAA has proved versatile for trace elements analysis in biological samples. Nigerian Research Reactor (NIRR-1) is particularly suitable for analysis of biological specimen because the average mean temperature at the irradiation channels is about 50°C thus leading to minimal volatilization losses. In addition INAA is highly sensitive, non-destructive and only requires minimum sample preparation of the specimen (Ahmed *et al*, 2010).

Materials and Methods

Sampling and Sample Preparation

(i) Three (3) locally tanned leathers bought from local tanners in the ancient city of Kano, and labeled LT (ii) three (3) leather samples collected from a tannery in Kano, and labeled GL (iii) three (3) samples collected from a popular craft market in Kano where leather materials are crafted for different uses, and labeled CM (iv) three (3) leather materials collected from a dump site where leather solid wastes are dumped by different tanneries and labeled DS.

A total of twelve (12) leather samples, were cut into small pieces and weighed using Mettler AE 240 analytical balance to obtain weights of between 0.3g-0.5g for each sample. Each sample was sealed in polythene bags pre-cleaned with distilled water and dilute HCl. Each polythene bag containing the leather samples was then secured inside sample vials (that were rinsed with distilled water and allowed to dry in an oven at a maintained temperature of 60°C for two hours), with sterilized cotton wool, covered and cello-taped, and set for irradiation.

Specimen Irradiation and Counting

The leather samples as contained in the irradiation vials were irradiated using the Nigeria Research Reactor-1 (NIRR-1) which is located at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria Nigeria. Since all of the determined elements produce long-lived nuclides, the irradiation was performed for 6 hours in the inner channels B2 where the magnitude of thermal neutron flux is the highest. After the irradiation, gamma-ray measurements were performed at sample–detector geometry of 1 cm for 60 minutes after a waiting period of 10 days. The choice of cooling time and sample-detector geometry were aimed at limiting dead time to less than 10%. A detailed description of the irradiation and gamma ray counting protocols for short and long irradiation for NIRR-1 as published by Jonah *et al*, 2006 is shown in table 2. Counting of induced gamma rays in the activation products were carried out using PC-based gamma-ray spectrometry set up which consists of a horizontal dip-stick High-Purity Germanium (HPGe) detector of relative efficiency of 10% at 133.5KeV, the MAESTRO emulation software compatible with the ADCAM$^{(R)}$ multi-channel analyzer (MCA) card, associated electronic modules and a personal computer. Identification of gamma-ray fingerprint of product radio-nuclides through their energies and quantitative analysis procedure for determination of their concentrations were achieved using the gamma-ray analysis software WINSPAN 2004 (Liyu, 2004).

Result and Discussion

Table 1 shows the analysis results for As, Br, Co, Fe, Rb, Sb and Zn in leather samples from Kano, Nigeria. In one of the samples from the dump site (DS3) and one sample (LT1) from the local tanners, Arsenic, (As) was determined as 4.6mg/kg and 3.5mg/kg respectively. The presence of As at the mg/kg range in one of the leather samples from the dump site may be as a result of possible association with other contaminants in the dump site. However, its concentration in one of the samples from local tanners may raise a question of how it came about. Although, Strauss *et. al*, (2006) stated that arsenic may be expected in leather. According to NOSB TAP Review (2000), arsenic was used to protect cattle from parasites in the past, and it is possible that this practice is still on in some countries and this could be a source of arsenic in hides. The limit set by the European Union (E.U) for Arsenic in leather is 25mg/kg (Ha, 2003). The Arsenic concentrations in samples DS3 (4.6mg/kg) and LT1 (3.5mg/kg) were both less than the 25mg/kg limit set by the EU.

Bromine (Br) was determined in some of the leather samples in the following concentrations: CM1 = 5.7mg/kg, CM2 = 1.7mg/kg, CM3 = 5.8mg/kg, GLT2 = 7.5mg/kg, GLT3 = 3.6mg/kg, LT2 = 2.1mg/kg. The cobalt (Co) concentrations in some of the samples were as follows: Samples DS3 = 0.5mg/kg, GLT2 = 1.8mg/kg, LT1 = 0.5mg/kg, LT2 = 1.9mg/kg, LT3 = 0.4mg/kg and CM2 = 1mg/kg. According to Strauss *et. al*, (2006), antimony (Sb), arsenic (As) and cobalt (Co) may be expected in leather.

Some of the metals can be found as impurities in industrial chemicals. Different leather dyes were analysed by Dyson (1979), and found that some of them were of cobalt complex. The presence of cobalt in some of the leather samples may be attributed to dyes that are used for leather finishing, since leather dyes may contain cobalt metal complex.

Relatively high concentrations of Fe were determined in samples: CM1 = 728mg/kg, DS1 = 609mg/kg, GLT1 = 2000mg/kg, GLT2 = 14000mg/kg, LT2 = 12000mg/kg. Kapel and Speak (1979) determined the concentration of Fe in five chrome tanned leathers with average value of 99mg/kg and in five vegetable tanned leather with average value of 663mg/kg. The work of Ferreira *et al*., (2000), also showed the presence of Fe in two leather ash samples (FGI = 13300mg/kg and FBI = 4890mg/kg) using XRF. For this work, the highest concentration of Fe was determined in sample GLT2 = 14000mg/kg, which was slightly higher than the FGI sample (13300mg/kg) by Ferreira *et. al*, (2003). The least concentration of Fe determined was in sample DS1 = 609mg/kg and unlike the work of Kapel and Speak, (1979) which showed higher concentration of Fe in vegetable tanned leather, this study showed the concentration of Fe to be highest in a chrome tanned leather sample (GLT2 = 14000mg/kg). Although the only vegetable tanned leather sample that indicated Fe (LT2 = 12000mg/kg) had a concentration higher than the Fe concentration of other chrome tanned leather samples (CM1 = 728mg/kg, DS1 = 609mg/kg, GLT1 = 2000mg/kg).

Rubidium (Rb) was determined in the following concentration in one of the samples, GLT1 = 26.8mg/kg. Also, antimony (Sb) was determined in sample LT2 as 0.6mg/kg. The detection limit for antimony using the INAA is 0.5mg/kg. It follows therefore that there may be Sb in other samples at concentration less than 0.5mg/kg. The elements; Sb and As are restricted heavy metals by the European Union (E.U). The limit set by EU for Sb in leather is 60 mg/kg (Ha, 2003). The concentration of Sb as 0.6 mg/kg in sample LT2 is a factor of 100 below the 60mg/kg limit set by the E.U.

The concentrations of Zn in a number of samples were as follows: DS1 = 60mg/kg, CM2 = 20.5mg/kg, CM3 = 12.3mg/kg, GLT2 = 119mg/kg, LT1 = 46mg/kg, LT2 = 33.2 mg/kg, LT3 = 46mg/kg. In a work carried out by Carneiro *et. al*, (2003), Zn as a metal was determined as 600mg/kg in the ash of chrome tanned leather scraps using AAS. In this study, the highest concentration of Zn was determined as 119mg/kg in sample GLT2 while the least concentration was determined as 12.3mg/kg in sample CM3.

Table1. Elemental concentrations in leather samples from Nigeria

Samples	Elements (mg/kg)						
	As	Br	Co	Fe	Rb	Sb	Zn
CM1		5.7±0.5		728±173			
CM2		1.7±0.3	1.0±0.2				20.5 ±3.6
CM3		5.8±0.5					12.3±3.6
DS1				609±160			60±6
DS2							
DS3	4.6 ± 0.6		0.5± 0.1				
GLT1				2000 ± 200	26.8 ± 5.1		
GLT2		7.5 ± 1.0	1.8 ± 0.4	14000±1000			119 ± 9
GLT3		3.6 ± 0.3					
LT1	3.5 ± 0.6		0.5 ± 0.1				46 ± 4
LT2		2.1 ± 0.2	1.9 ± 0.2	12000± 1000		0.6 ± 0.1	33.2 ± 0.1
LT3			0.4 ± 0.1				46 ± 4

Table 2 Routine irradiation and measuring regimes developed for NIRR-1 facilities.

Neutron flux/irradiation channel	procedure	T_{irr}	Td	Tm	Activation products
$1x10^{11}$n/cm^{2}s/outer irradiation channels (B4, A2)	S1	2min	2-15min	10min	^{28}Al,^{27}Mg,^{38}Cl,^{49}Ca, ^{66}Cu,^{51}Ti,^{52}V,^{116m}In
	S2	2min	3-4hrs	10min	^{24}Na,^{42}K,^{165}Dy,^{56}Mn, ^{152m}Eu
$5x10^{11}$n/cm^{2}s/inner irradiation channels (B1, B2, B3 and A1)	L1	6hrs	4-5days	30min	^{24}Na,^{42}K,^{76}As,^{82}Br, ^{153}Sm,^{140}La,^{198}Au ^{239}Np(U),^{72}Ga,^{122}Sb
	L2	6hrs	10-15days	60min	^{46}Sc,^{141}Ce,^{60}Co,^{51}Cr, ^{134}Cs,^{152}Eu,^{177}Lu, ^{131}Ba,^{86}Rb,^{182}Ta,^{160}Tb, ^{175}Yb,^{233}Pa(Th),^{65}Zn, ^{59}Fe,^{181}Hf

Source: (Jonah, *et. al,* 2006).

Conclusion

Neutron Activation Analysis has been used to determine As, Br, Co, Fe, Rb, Sb and Zn in 12 leather samples. The results of some of the elements compare well with earlier works by others. However, in this study, the highest concentration of Fe was recorded for vegetable tanned leather sample, unlike in the work of Kapel and Speak, (1979) which recorded the highest concentration of Fe in a sample of chrome tanned leather. In 2 out of the 12 samples analysed, As was determined; whereas Sb was determined in 1 of the samples. Although the two elements As and Sb are of toxicological concern, their concentrations in some of the leather samples analysed, were below the set limit by E.U and may therefore be termed safe.

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