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Research Article

DETERMINATION AND THE EFFECT OF PROCESSING ON THE PRESENCE OF TOXIC METALS IN EDIBLE OILS AND GHEE CONSUMED IN KOHAT, KHYBER PAKHTUNKHWA

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ABSTRACT

Ghee and oil is one of the important ingredients of food especially in south Asian region. Heavy metals are one of the potential hazards associated with food. Different oil and ghee samples were collected from the local Market, the samples of different processing stages were collected from a local ghee industry while the raw samples were collected directly from field. The aim of the study was to determine and compare the variation in concentrations of heavy metals in ghee, fractions of ghee, raw oil and commercially available edible oils. The metals were analyzed by atomic absorption spectrometry after acid digestion. The concentrations for nickel, copper, iron, zinc, and lead were observed in the range of 0.013–1.01, 0.02-0.1, 0.157-1.14, 0.469-2.48, 0.006-0.024 ppm respectively. The highest nickel content (1.01ppm) was found in hydrogenated fraction of ghee however, the concentrations of metals decrease during different stages of oil refining. It was observed that the processing may add to the contamination of heavy metals along with the anthropogenic activities in the environment.

INTRODUCTION

Oil and ghee is an essential portion of our daily use. The human body utilizes ghee and oils as a source of energy, as a structural constituent and to make biological regulators. Any adulteration in these sources will be directly accumulated in the body, producing various complications depending upon the nature of toxicity. The main sources of the adulteration in the oils and ghee are the processing such as bleaching, hardening, refining and deodorization or by metal contaminated equipments and storage of these items. Ni is used as catalyst for the hydrogenation of ghee while similar metal packed containers are used for the storage and transportation of oil and ghee which can be a rich source of contamination. The metals might also come from the soil by deposition as well as bioaccumulation of naturally occurring metal sources and environmental pollution. Some metals such as Fe or Mn can increase the rate of fatty acids oxidation hence affecting the quality of edible oils and ghee while other metals such as Zn, Cu, Ag, Hg, and Pb can affect the metabolic process of the body. The oxidation of fatty acids due to heavy metal contaminants produces epoxides, aldehydes, ketones and acids which have pathological effects on the digestive system (Llorent-Martínez, Ortega-Barrales *et al*. 2011).

Heavy metals are persistent and do not decompose in the environment and are magnified biologically through the ecological food chain. These metals bio accumulate at primary producer level and then finally transported to consumer level by their consumption. Heavy metals have adverse effects on human health when consumed above the recommended limits. Metals such as cadmium, mercury, lead and arsenic etc causes gastrointestinal disorders, tremors, hemoglobinuria, ataxia, paralysis, vomiting, pneumonia etc. The effects of heavy metals could be (acute or chronic), carcinogenic, mutagenic and neurogenic (Duruibe, Ogwuegbu *et al*. 2007).

The heavy metals can be removed by means of magnetic trap or a filtration. In the classical refining process the heavy metal ions are partially removed by degumming, by using cation exchange resin or by using acid washing step (Keurentjes, Bosklopper *et al*. 1990). No work is reported on the presence of toxic metals in the oils and ghee consumed in the Khyber Pakhtunkhwa specially in Kohat. The aim of the present work is to determine the presence of various toxic elements in the edible oil and ghee used in the region and also to compare the toxic metals concentration in processed edible oils and raw oils.

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MATERİALS AND METHODS

Sample collection

Sampling was carried out in two different ways, initially various oil and ghee samples were collected from local market and then seeds of several oil containing plants like canola, mustard, sunflower were collected from different regions of Pakistan. Oils were extracted from seeds by solvent extraction method. The samples were also collected from the ghee industries before and after processing.

Sample preparation

1g sample of each edible oil and ghee samples were accurately weighed. About 10 ml of a freshly prepared mixture of concentrated HNO_3:H_2O_2 (2:1 v/v) were added to each sample in flask and kept for 10 min at room temperature, then the content of flasks were heated on an electric hot plate at 80 °C. The contents of the flasks were evaporated, and the semidried mass was dissolved in 5 ml HNO_3, filtered through whatman filter paper, and diluted upto 25 ml final volume in volumetric flasks with ultrapure water and kept as stock sample solution.

Sample Analysis

The edible oil and ghee samples were analyzed for the selected heavy metals like, Nickel (Ni), Lead (Pb), Zinc (Zn), Copper (Cu) and Iron (Fe) through Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

Spike sample analysis

Spike sample analysis is used to test the method at varying concentrations of analyte. Known amounts of analyte are added to a sample and the recovery values are calculated. In order to validate data spike recovery tests were performed by adding 2.0 and 4.0 ppm of each metal to different samples. The results were obtained as the mean of three replicates of each sample and are shown in Table 1. As can be seen, the method has good precision and the recoveries were between 92% and 100%. The proposed method was applied to Pb, Cu, Fe, Ni and Zn determination in edible oils, ghee fractions and ghee samples.

Table 1 Recoveries (%) for spiked sample

Element Sample		**Spiked concentration, ppm**	
		2.00	4.00
Edible Oils	Cu	99 0±0 11	100 ±0 4
	Fe	98 0±0 2	95 0±0 6
	Ni	93 0±0 4	100 ±0 4
	Pb	97.0±02	98.0±03
	Zn	96.0±0 2	98 0±0 2
Ghee	Cu	99 0±0 4	92 0±0 2
	Fe	98 0±0 5	95 0±0 3
	Zn	97 0±0 3	98 0±0 2
	Ni	99.0 ±0 5	90 0±0 3
	Pb	98.0±04	99.0±03

Trace amount of nickel content may be beneficial as an activator of some enzyme but its toxicity is more prominent at higher level. The nickel content in our investigated samples ranges from 0.013–1.01ppm. The presence of a small amount of nickel in raw oils may be attributed due to endogenous factors concerned with the uptake of different heavy metals by plant roots to stem, leaves and their ultimate translocation to the seeds or exogenous factors due to possible contamination of seeds by environmental pollution. The highest nickel content (1.01ppm) was found in hydrogenated fraction of ghee because nickel was used as hardening or hydrogenating agent for the conversion of glycerides of unsaturated fatty acid to saturated fatty acid of another series, however the concentrations of metals decreases during different stages of oil refining. According to the international and national requirements, the approved content of nickel (Ni) in edible oils and ghee was 0.2 ppm (Kowalewska, Izgi *et al*. 2005). The nickel values in the investigated oils and ghee samples were in agreement with the maximum acceptable limits (0.2ppm).

Table 2 Nickel concentration in edible oils and ghee

Sample Description		Concentration of Ni in Blank	Concentration of Ni in Edible oil samples
Mustard Oil	A	N.D	0.035±0.006
	B		0.027±0.003
	C		0.056±0.004
Sunflower Oil	A	N.D	0.044±0.002
	B		0.061±0.005
	C		0.059±0.011
	D		0.035±0.002
	E		0.078±0.007
Canola Oil	A	N.D	0.039±0.014
	B		0.026±0.012
	C		0.055±0.016
	D		0.069±0.009
	E		0.073±0.013
Raw oil	A	N.D	0.013±0.008
	B		0.022±0.005
	C		0.031±0.017
	D		0.034±0.022
	E		0.018±0.015
	F		0.028±0.019
Ghee Samples	A	N.D	0.14±0.021
	B		0.15±0.017
	C		0.2±0.016
	D		0.1±0.011
Ghee Fractions	B.F	N.D	0.023±0.007
	H.F		1.01±0.008
	F.P		0.19±0.004

Copper is an essential heavy metal for good health but excessive intake of copper may lead to severe health problems such as kidney and liver disorders (Ikem and Egiebor 2005). Copper deficiency leads to leucopenia, osteoporosis in children and hypochromic anaemia (Kanumakala, Boneh *et al*. 2002). Copper is well-known for its toxicity and vitality for many biological systems. The concentration of copper was observed in our investigated samples of oil and ghee in the range of 0.02-0.1ppm. According to international and national standards, the permitted contents of these metals in edible oils and ghee samples are: 0.1 ppm (Cu, Pb, As), 1–1.5 ppm (Fe), 0.2 ppm (Ni) and 0.05ppm (Cd) (Kowalewska, Izgi *et al*. 2005). The copper content in our investigated oils and ghee samples were in agreement with those reported by (Zhu, Fan *et al*. 2011) .

Table 0 Copper concentration in edible oils and ghee

Sample Description		Concentration of Cu in Blank	Concentration of Cu in Edible samples
Mustard Oil	A	N.D	0.063±0.002
	B		0.085±0.007
	C		0.071±0.005
Sunflower Oil	A	N.D	0.092±0.012
	B		0.087±0.008
	C		0.089±0.011
	D		0.064±0.016
	E		0.07±0.009
Canola Oil	A	N.D	0.083±0.005
	B		0.09±0.008
	C		0.087±0.006
	D		0.067±0.001
	E		0.072±0.004
Raw oil	A	N.D	0.023±0.011
	B		0.02±0.017
	C		0.05±0.021
	D		0.034±0.023
	E		0.044±0.019
	F		0.059±0.016
Ghee Samples	A	N.D	0.056±0.012
	B		0.1±0.009
	C		0.078±0.008
	D		0.1±0.004
Ghee Fractions	B.F	N.D	0.06±0.017
	H.F		0.078±0.021
	F.P		0.083±0.026

N.D= Not detected B.F=Bleached Fraction
H.F=Hydrogenated Fraction F.P=Final Product

Sufficient amount of iron in our diet is necessary for decreasing the incidence of anaemia (Ashraf and Mian 2008). Iron deficiency is commonly associated with anaemia and thus, decreases working power and damaged intellectual development (Schümann, Ettle *et al*. 2007). The lowest iron content (0.157ppm) was observed in our investigated raw oil extracted from sunflower seeds while the highest iron

Table 4 Iron concentration in edible oils and ghee

Sample Description		Concentration of Fe in Blank	Concentration of Fe in Edible oil and ghee samples
Mustard Oil	A	N.D	0.66±0.008
	B		0.28±0.005
	C		0.9±0.003
Sunflower Oil	A	N.D	1.01±0.001
	B		1.1±0.006
	C		0.60±0.011
	D		0.79±0.009
	E		1.05±0.017
Canola Oil	A	N.D	1.09±0.026
	B		1.00±0.021
	C		0.87±0.023
	D		1.08±0.019
	E		1.14±0.016
Raw oil	A	N.D	0.54±0.009
	B		0.65±0.013
	C		0.9±0.008
	D		0.157±0.004
	E		0.59±0.015
	F		0.88±0.012
Ghee Samples	A	N.D	1.04±0.007
	B		1.06±0.016
	C		1.02±0.025
	D		1.12±0.021
Ghee Fractions	B.F	N.D	0.98±0.026
	H.F		1.06±0.020
	F.P		1.00±0.022

N.D= Not detected B.F=Bleached Fraction
H.F=Hydrogenated Fraction F.P=Final Product

concentration (1.14ppm) was observed in commercially processed canola oil. The presence of iron content in commercially available edible oils and ghee samples may be due to the reaction between the relatively high-unsaturated portion of the oil with the surface of iron containers to be used during transportation, storage and processing of oils and fats or due to natural sources. According to the national and international standards for Fats and Oils the approved iron content in vegetable oils and fats is 1-1.5ppm (Zhu, Fan *et al*. 2011). Iron concentration in our investigated edible oil samples were within range of the approved limits.

Zinc is common among living organisms due to its biological importance. Zinc is involved in most of the metabolic pathways in humans and its scarcity can lead to immunological abnormalities, growth retardation, and loss of appetite and skin changes. The zinc concentration in analyzed samples ranged from (0.469 to 2.48ppm). Raw oil extracted from (canola seeds) has the lowest zinc level whereas commercially available canola oil has the highest. The minimum concentration in raw oil may be due to the unavailability of zinc in the soil while maximum concentration in canola oil may be attributed to the processing (bleaching, degumming, deodorization etc) .The obtained results declared that the amount of Zn in edible oil and ghee samples was within recommended international standards. The FAO/WHO has set a limit for heavy metal intake based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for iron , lead, copper and zinc are 48ppm, 0.214ppm, 3ppm and 60 ppm respectively. The zinc level in our investigated oil and ghee samples were also in agreement with those reported by Z. Fangkun (Zhu, Fan *et al*. 2011).

Table 5 Zinc concentration in edible oils and ghee

Sample Description		Concentration of Zn in Blank	Concentration of Zn in Edible oil samples
Mustard Oil	A	N.D	1.11±0.012
	B		1.6±0.09
	C		2.41±0.02
Sunflower Oil	A	N.D	2.3±0.06
	B		2.29±0.014
	C		1.61±0.016
	D		0.89±0.012
	E		2.3±0.019
Canola Oil	A	N.D	2.17±0.026
	B		1.01±0.07
	C		0.9±0.011
	D		1.34±0.015
	E		2.48±0.022
Raw oil	A	N.D	1.98±0.017
	B		0.56±0.008
	C		2.35±0.031
	D		1.09±0.018
	E		0.572±0.007
	F		0.459±0.004
Ghee Samples	A	N.D	0.894±0.006
	B		1.4±0.008
	C		0.79±0.011
	D		2.0±0.013
Ghee Fractions	B.F	N.D	1.06±0.013
	H.F		1.09±0.015
	F.P		1.7±0.012

N.D= Not detected B.F=Bleached Fraction
H.F=Hydrogenated Fraction F.P=Final Product

Lead has no important role in human metabolism. It was well-known for its chronic and acute poisoning which may lead to failure to the heart, liver, kidney and immune system. Long term exposure to such metal also causes cancer, chromosome aberration, and birth defect. Lead also creates disorders such as tiredness, sleeplessness, hear and weight loss. The concentration of lead in edible oil and ghee samples were observed in the range of 0.006-0.024ppm. The presence of lead concentration could be due to deposition or bioaccumulation from the soil phosphate base fertilizer (Ansari, Kazi *et al*. 2009) that was used in the plantation or may be due to water used for irrigation whereas maximum lead content in canola oil may be due to industrial emission, combustion of fuel in refinery process, and from packaging material such as stabilizer and colorant in plastic (Dugo, La Pera *et al*. 2004). According to Codex Alimentarius and national standards the permissible concentration of Lead (Pb) in fat and oils is 0.1ppm (Lacoste 2014). The result shows that the mean concentration of lead in edible oils and ghee samples was within the recommended permissible standards.

Table 6 Lead concentration in edible oils and ghee

Sample Description		Concentration of Pb in Blank	Concentration of Pb in Edible oil samples
Mustard Oil	A	N.D	0.014±0.002
	B		0.022±0.003
	C		0.01±0.007
Sunflower Oil	A	N.D	0.024±0.014
	B		0.011±0.011
	C		0.02±0.018
	D		0.007±0.016
	E		0.022±0.015
Canola Oil	A	N.D	0.024±0.009
	B		0.02±0.004
	C		0.014±0.002
	D		0.021±0.002
	E		0.017±0.003
Raw oil	A	N.D	0.01±0.006
	B		0.015±0.003
	C		0.006±0.007
	D		0.019±0.012
	E		0.013±0.011
	F		0.008±0.005
Ghee Samples	A	N.D	0.019±0.02
	B		0.013±0.016
	C		0.02±0.017
	D		0.016±0.011
Ghee Fractions	B.F	N.D	0.015±0.004
	H.F		0.023±0.007
	F.P		0.02±0.008

N.D= Not detected B.F=Bleached Fraction
H.F=Hydrogenated Fraction F.P=Final Product

The results of the analyzed samples shows that the heavy metals concentration varies from minimum to maximum in the raw oil and processed edible oils and ghee samples. This contamination may be due to natural sources, environmental pollution, utensils used or may be process related but results obtained were within the permissible limits.

CONCLUSION

The results show that the toxic metal concentration increases with the processing, handling and transportation and also is directly linked with environmental factors. The samples of oils and ghee analyzed have the some presence of the heavy metals but that is within limit of who and so has no hazardous effects on health.

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