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Determination of Copper, Manganese, Nickel and Zinc in Different Cigarette Brands Available in Pakistan

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Abstract. Mean values of copper, manganese, nickel and zinc in different cigarette brands sold in Pakistan were found to be in the range of 8.61 to 94.67 μg/g, 26.40 to 98.20 mg/g, 0.61 to 8.58 mg/g and 16.92 to 99.60 mg/g, respectively, through Atomic Absorption Spectrophotometer (AAS). The results are discussed with reference to and in comparison with the mean average concentration of these elements reported in the cigarettes of other countries.

Keywords: cigarette, tobacco, smoking, heavy metals, health effect

Introduction

Tobacco products, such as cigarettes and cigars are known to pose a serious environmental health threat to consumers themselves and to the people around them as well. Cigarette is one of the means by which nicotine in tobacco is consumed by humans. Approximately 5 trillion cigarettes are produced each year or 1,000 cigarettes per man, woman or child (HRO/World, 2003). Usually, cigarette is made up of tobacco, paper and additives. Cigarette smoke contains both organic and inorganic compounds that are human carcinogens. Therefore, knowledge of the nature and quantity of elements present in the tobacco is imperative for human safety. Studies have been carried out in various countries to monitor the contents of local brands of cigarettes (Ciftci and Olcuca, 2007; Massadeh *et al.,* 2003; Jung *et al.,* 1998; Mussalo-Rauhamaa *et al.,* 1986). Uptil now about 4000 compounds, including heavy/trace metals, have been identified in the tobacco smoke and most of them are harmful to human beings (Nnorom *et al.*, 2005). Injurious effects of smoking on health are also correlated with the intake of heavy metals present in the mainstream smoke (inhaled by smoker during a puff), side stream smoke (smoke produced mainly between the puffs) and the butt and the ash of the cigarettes.

According to Mussalo-Rauhamaa *et al.* (1986), on an average 0.2% Cu and 1% Zn contained in the cigarette pass into the mainstream smoke. Menden *et al.* (1972) reported that 0.4 - 2.4% of Ni in the smoked portion of cigarettes appears in the mainstream smoke, whereas, 11-33% of Ni is found in side stream smoke. Thus, heavy metals in both the mainstream smoke and side stream smoke of cigarettes may have adverse effects on health of non-smokers as well as smokers.

Copper is the third most important trace element in the body, following zinc and iron (Kaplan *et al.,* 1993). A lot of disorders are associated not only with the toxic effects of copper accumulation in the tissues, such as liver, brain, cornea and kidney but also with the copper deficiency. These disorders include Wilson's disease, Menkes disorder and Indian childhood cirrhosis (Massadeh *et al.,* 2003). Zinc is required at many stages of fetal growth and development. Massadeh *et al.* (2003) reported that pregnant smokers have higher levels of Zn in the placenta while their infants have significantly lower level of Zn in the red blood cells.

During the last two decades, different techniques have been used for the determination of inorganic constituents particularly that of heavy metals in tobacco of different brands of cigarettes of various countries (Massadeh *et al.,* 2003; Csalari and Szantai, 2002; El-Agha and Gokmen, 2002). Main objective of this study was to measure the concentrations of Cu, Mn, Zn and Ni in different cigarette brands available in Pakistan and to estimate their amount inhaled through consumption of these cigarettes.

Materials and Methods

Sample collection. Samples of 24 brands of cigarettes commonly available in Pakistan, were purchased from retail outlets in Karachi. Three samples of each variety of cigarettes were collected from different areas and analysed for copper, manganese, nickel and zinc.

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Apparatus. Hitachi Z-8000 atomic absorption spectrophotometer equipped with Zeeman effect background correction, a microprocessor and a built-in printer was used for determination of Cu, Mn, Ni and Zn, employing the standard addition technique. Measurements were made by using hollow cathode lamp.

Reagents and solutions. The standard metal solutions of Cu, Mn, Ni and Zn (1000 mg/litre; analytical grade, Merck) were diluted to the desired concentrations with deionized water. Concentrated (ultra pure grade, Merck) HNO_3, $HClO_4$, H_2O_2 and deionized distilled water were used for digestion of cigarette samples.

Preparation of sample solution. Different weights of all tobacco samples were dried in oven at a temperature of 80 ± 1 °C for 6 h and allowed to cool in desiccator. The dried samples were dissolved in an acid mixture containing 10 ml of 65% HNO_3 and 4 ml of 60% $HClO_4$ so that organic matter was decomposed and metal ions changed into respective nitrates. The mixture was then filtered using Whatman filter paper # 42 into a volumetric flask and made up to mark by adding deionized water.

Analysis of sample solution. Determination of Cu, Mn, Ni and Zn in cigarette samples was carried out at by Hitachi Z-8000 ASS with Zeeman correction using air acetylene flame with standard addition methods (Clesceri *et al.,* 1998).

Sample solutions were analysed using the method of direct calibration curve by flame atomic absorption spectrometry (FAAS); for Ni, flameless atomic absorption spectrometry was used. Triplicate readings were taken for each sample. Working conditions for the elements detected by atomic absorption spectrophotometer are presented in Table 1.

Accuracy was also monitored by spike with Cu, Mn and Zn at the level of 1.0 mg/litre each, and Ni at the level of 20 µg/litre. Five cigarette samples were spiked with Cu, Mn, Ni and Zn to determine the recovery. The average recovery is given in Table 2.

Table 1. Working conditions for the detected elements by AAS

Parameters	Cu	Mn	Ni	Zn
Slit (unit)	1.3	0.4	0.2	1.3
Wave length (nm)	324.8	279.3	232.0	213.8
Drying temperature (°C)	80-120	80-120	80-120	80-120
Ashing temperature (°C)	600	500	700	300
Atomization temperature (°C)	2700	2500	2700	2000

Calibration curves for elements. Readings were always taken in the linear range. Concentrations were determined using the best line equations. Calibration curves are shown in Fig. 1.

Table 2. Recovery of metals added to the cigarettes

Elements	Spike level	No. of samples	Observed values	Recovery (%)
Cu	1.0 mg/litre	5	0.996	99.6
Mn	1.0 mg/litre	5	0.980	98.0
Ni	20 µg/litre	5	19.1	95.5
Zn	1.0 mg/litre	5	0.972	97.2

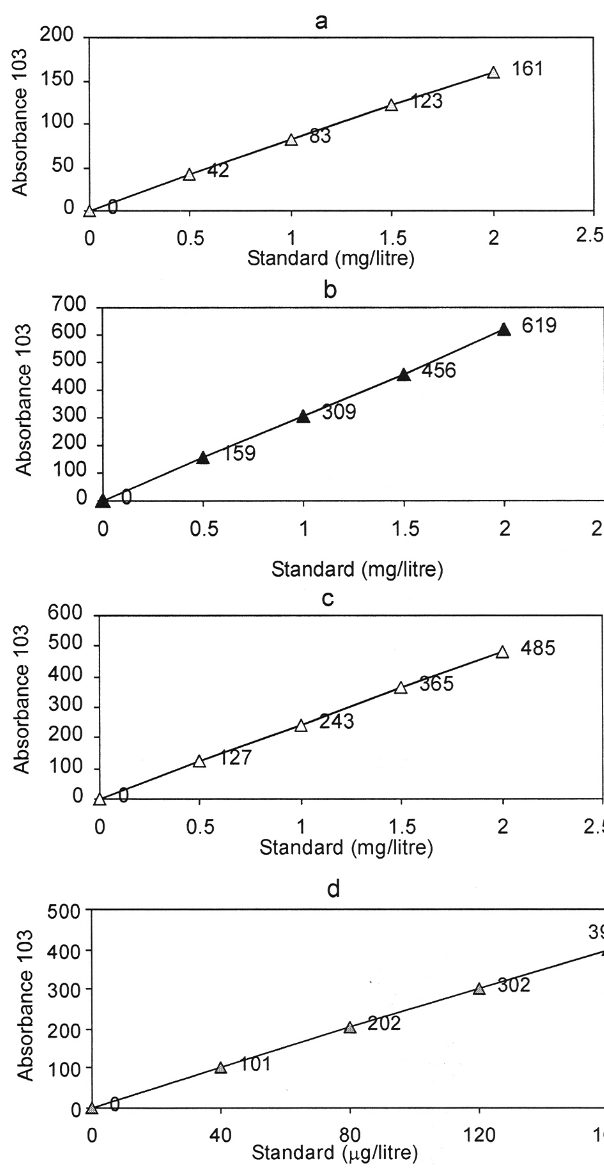

Fig. 1. Calibration curves for (a) Cu (b) Mn (c) Zn and (d) Ni.

Results and Discussion

The concentration level of metal ions in the cigarettes, determined in mg/g by AAS, is presented in Table 3. The generated data was compared with the data collected earlier from various countries (Table 4).

Weight of cigarette varies with the length of the cigarette. For normal cigarette length of 8.2 to 8.9 cm with filter, the weight ranges from 0.85 to 1.11 g/cigarette, whereas, the weight of long cigarettes (10 -12 cm in length) ranges from 0.55 to 1.01 g/cigarette.

Many studies on Cu concentration in cigarettes have been undertaken in various countries (Table 4). Mussalo-Rauhamaa *et al.* (1986) reported that Cu in cigarette samples from Finland averaged 15.6 mg/g in the range of 9.20-17.6 mg/g. A similar study of cigerettes of different countries revealed the mean concentration of Cu to be 13.0 mg/g in the range of 8.92-20.3 mg/g in the UK; less than 10 (7.73) mg/g in the range of 5.96-11.4 mg/g in the Korean cigarettes (Jung *et al.,* 1998) and mean concentration of Cu to be 24.58 mg/g in the range of 18.4-30.8 mg/g in the Turkish cigarettes (Ciftci and Olcucu, 2007). Copper concentration in Jordanian cigarettes averaged 12.92 mg/g, range being 11.37 to 14.42 mg/g (Massadeh *et al.*, 2003). In this study, the mean average concentration of Cu was recorded in the range of 8.61-94.67 mg/g with the mean value of 29.478 mg/g (Table 3) which is higher than the values reported for Finland, Korea, UK, Turkey and Jordan.

Concentration of Zn in different brands of cigarettes from various countries had been reported to be in the range of 30-50 mg/g. In the cigarette samples of Finland the concentration of Zn was in the range of 38.0-54.0 mg/g (Mussalo-Rauhamaa *et al.,* 1986), in Korean cigarettes in the range of

Table 3. Weight and concentration of Cu, Mn, Ni and Zn in 24 brands of cigarette available in local markets in Pakistan

Cigarette code	Weight (g/cigarette)	Cu (mg/g)	Mn (mg/g)	Ni (mg/g)	Zn (mg/g)
PK01	0.9542	24.78 ± 0.00	69.9 ± 0.01	3.64 ± 0.00	46.42 ± 0.02
PK02	0.9886	94.67 ± 0.00	64.88 ± 0.02	5.39 ± 0.2	70.30 ± 0.01
PK03	0.8798	38.64 ± 0.01	28.02 ± 0.01	2.43 ± 0.00	46.90 ± 0.01
PK04	1.1132	11.04 ± 0.00	63.28 ± 0.03	4.34 ± 0.3	34.50 ± 0.04
PK05	0.8778	8.61 ± 0.01	83.80 ± 0.00	3.71 ± 0.8	60.20 ± 0.03
PK06	1.0110	78.09 ± 0.05	62.50 ± 0.00	3.62 ± 0.0	49.80 ± 0.02
PK07	0.9298	36.56 ± 0.00	26.40 ± 0.01	0.61 ± 0.6	26.50 ± 0.00
PK08	0.9495	24.64 ± 0.00	47.92 ± 0.00	3.26 ± 0.6	39.40 ± 0.02
PK09	0.9041	12.11 ± 0.00	77.42 ± 0.02	8.58 ± 0.9	16.92 ± 0.00
PK10	0.9551	10.36 ± 0.01	98.20 ± 0.02	5.19 ± 0.1	52.90 ± 0.07
PK11	0.8931	11.86 ± 0.01	46.91 ± 0.00	2.71 ± 0.2	39.40 ± 0.02
PK12	0.8839	74.83 ± 0.00	96.78 ± 0.00	4.82 ± 0.3	94.19 ± 0.04
PK13	0.8926	37.02 ± 0.01	54.16 ± 0.02	3.67 ± 0.3	41.22 ± 0.00
PK14	0.8585	12.4 ± 0.01	95.94 ± 0.02	2.17 ± 0.3	36.38 ± 0.00
PK15	0.9929	12.53 ± 0.00	70.15 ± 0.01	2.86 ± 0.6	99.60 ± 0.00
PK16	0.9552	33.02 ± 0.03	88.56 ± 0.01	2.08 ± 0.3	42.80 ± 0.02
PK17	1.0518	13.31 ± 0.00	61.56 ± 0.00	2.49 ± 0.5	28.30 ± 0.01
PK18	0.9894	46.59 ± 0.00	68.42 ± 0.01	1.68 ± 0.0	35.60 ± 0.00
PK19	1.0116	12.35 ± 0.00	61.78 ± 0.02	2.78 ± 0.1	39.49 ± 0.02
PK20	1.1082	29.59 ± 0.01	57.02 ± 0.00	2.93 ± 0.5	73.50 ± 0.03
PK21	0.9646	9.17 ± 0.01	97.60 ± 0.00	3.46 ± 0.9	64.40 ± 0.00
PK22	0.5507	10.62 ± 0.00	45.5 ± 0.04	7.25 ± 0.0	95.10 ± 0.02
PK23	1.0199	41.18 ± 0.01	96.23 ± 0.01	2.35 ± 0.1	58.87 ± 0.03
PK24	0.9148	23.5 ± 0.01	62.19 ± 0.00	2.84 ± 0.8	39.20 ± 0.00
Mean	0.944	29.478	67.724	3.537	51.331
Maximum	1.113	94.67	98.205	8.588	99.602
Minimum	0.551	8.61	26.4	0.615	16.92

Table 4. Concentrations of heavy metals contents in the cigarettes studied and reported for some other individual countries

Element	Country	No. of samples	Range (mg/g) tested	Mean value (mg/g)	Reference
Cu	Finland	11	9.2-17.6	15.6	Mussalo-Ruhamaa *et al*
	Korea	14	5.96-11.4	7.73	Jung *et al*
	UK	10	8.92-20.3	13	Jung *et al*
	Turkey	05	18.4-30.8	24.58	Ciftci and Olcucu
	Jordan	19	11.37-14.42	12.92	Massadeh *et al*
	Pakistan	24	8.6-94.67	29.5	Present study
Mn	Pakistan	24	26.46 98.20	67.72	Present study
Ni	Pakistan	24	0.61-8.58	3.54	Present study
Zn	Finland	11	38-54	49.7	Mussalo-Ruhamaa *et al*
	Korea	14	34.6-46.1	38.5	Jung *et al*
	UK	10	26.6-36.0	31.9	Jung *et al*
	Turkey	05	16.2-61.8		Ciftci and Olcucu
	Jordan	19	45.6-65.58	55.62	Massadeh *et al*
	Pakistan	24	16.9-99.6	51.33	Present study

34.6-46.1 mg/g (Jung *et al.,* 1998), in British cigarettes in the range of 26.6-36.9 mg/g, which is relatively lower than Finland, whereas, in Turkish cigarettes, the concentration of Zn was in the range of 16.2-61.8 mg/g, being higher than that of Finland, Korea and U.K. The concentration of Zn in Jordanian cigarettes averaged 55.62 mg/g in the range of 45.6 to 65.58 mg/g. The level of Zn in the cigarette samples recorded in the present study was in the range of 99.602 to 16.92 mg/g with the mean value of 51.331 mg/g, which is higher than that reported for the cigarettes of other countries.

Little information on the concentration of other elements including Mn and Ni in foreign brands of cigarette is available at present. In the present study, concentrations of Mn and Ni in the cigarette samples was in the range of 98.205-26.4 and 8.588-0.615 mg/g with the mean value of 67.724 and 3.537 mg/g, respectively.

Cigarette smoking is an advantageous delivery system for nicotine, which accelerates and aggravates cardiovascular diseases and is usually associated with the increased risk of chronic obstructive lung diseases, lung cancer and upper aerodigestive system. Cigarette smoke impairs both male and female fecundity and may potentiate the effects of other suspective reproductive toxicants like caffeine (Benoff *et al.,* 2000; Hoffman and Hoffman, 1997).

Tobacco kills some 3 million people each year, thus ranking it with AIDS as one of the world's leading killers (HRO/ WHO, 2003). Due to cardiovascular stress caused by carbon monoxide in smoke leading to chronic bronchitis and emphysema, about twice as many people die of heart failure as from lung cancer associated with smoking (Cunningham *et al.,* 2005). In India, tobacco use has been associated with worse nutrition and worse child health outcome (Shukla *et al.,* 2002).

Conclusion

Tobacco consumption through cigarette is a problem assuming an alarming proportion in the world. This study shows that the level of Cu, Mn, Ni and Zn in the cigarettes available in Pakistan compares well with the levels of those from other parts of the world. The data obtained through this study will be valuable in complementing the available data on intake of Cu, Mn, Ni and Zn due to cigarette smoking and in estimating dietary intake of heavy metals in Pakistan. Efforts should be made by the government at discouraging the consumption of cigarettes.

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