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Metal Distribution in Pakistani and Foreign Brands of Cigarette Ash

S. Zulfiqar, S. Shabbir, M. Ishaq, M. S. Shaukat, M. I. Sarwar

Department of Chemistry, Quaid-i-Azam University, Islamabad, 45320, Pakistan

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Cigarette ash plays an important role in terms of toxic trace metal distribution towards human health and environmental pollution. Ash is a grayish white to black powdery residue left when cigarette is burnt. The ash region is part of the combustion zone that experiences temperatures around 400ºC (Liu and Woodcock 2002). Baliga et al. (2004) reported that elements measured from the control unburned tobacco, the coal base, coal tip and ash regions showed stability of some elements and volatility of others. Although the ash resulting from the tobacco of a cigarette is only a fraction of the amount of tobacco, yet it is a critical component in the spread of heavy metals in the open atmosphere. It is believed that ash particles are less than 2 micron in size, and various studies conducted in advanced countries of the world have suggested that this particle size must be warded off to control the adverse effects of the ash particles on human respiratory system. Ash particles of the order of 2 micron are directly deposited in the air sacs and air pathways in the lungs, terminating into solubilized metals leached out in various aqueous and non-aqueous fluids with in the human body. Lung cancer is one probable aspect for such an effect of ash on humans. The degree of severity associated with the ingestion of ash is related to its amount irrespective of the brand of cigarette.

Studies indicate that there is a definite correlation between the level of trace elements in the human body and some diseases (Ahmed et al. 1979). Iskander (1986) has shown that heavy metals are toxic for the human bio system even at very low levels of intake. Therefore, it is necessary to measure these trace elements in ash for assessing the possible role they may play to cause some diseases. Adverse health effects associated with indoor air pollutants are from cigarette smoking in the form of particulates (Morawska and Zhang 2002). A major pathway for these particulates to human via inhalation and respiratory system has been identified as their major point of attraction. So, there is a need for

Correspondence to: M. I. Sarwar

a good knowledge of their physical and chemical properties for adequate air quality regulations (Vedal 1997). Salma et al. (2002) reported the distribution pattern of these particulates in the human respiratory system under sitting breathing condition using a stoichiostic lung deposition model earlier developed by Wallace et al. (1997) to calculate the deposition of ambient aerosols for human health implication prediction. Ebisike et al. (2004) reported that the concentrations of Zn, Cu and Cd in tobacco were higher than those in the ash. During combustion activity which results in ash formation, some of these metals could have been produced in free form due to the breaking down of their compounds. Jordanova et al. (2005) investigated the magnetic behavior of cigarette ashes proving the non-negligible magnetic properties of these plant ashes.

The main objective of this work is to evaluate and compare the status of heavy toxic trace metal pollution arising from cigarette ash and to determine the potential harm they constitute to the environment. Keeping in view the serious health impacts, this study is aimed at assessment of levels of heavy metals like Ni, Cd, Cr, Zn, Pb and Cu in ash of various Pakistani and foreign brands of cigarette. In this attempt, correlation for pairs of metals in terms of their origin and distribution in atmosphere has been determined. It is anticipated that this work could be used as an incentive to develop strategies for controlling ash related environmental issues.

MATERIALS AND METHODS

Heavy toxic trace metals (Ni, Cr, Zn, Cd, Pb and Cu) were analyzed in thirty cigarette ash samples, 15 each of Pakistani and foreign brands obtained from local vendors. Related information on sample codes and description of make for both versions is given in the Table 1 and 2. A unit cigarette along with the wrapper (filter portion cut away) was converted into ash by just igniting its tip and allowing it to undergo combustion on its own, ultimately sizzling down to an ash which was weighed out for further metal quantification. Using wet digestion method, this known mass of ash sample was digested in 4:1 (v/v) $HNO_3/HClO_4$ mixture (NIOSH Method-7300, 1984).

A Shimadzu Atomic Absorption Spectrophotometer (AA-670 Japan) was used for the estimation of metal levels. Blanks were simultaneously run for each metal with approximately <10% blank level of the estimated metal concentrations. All reagents used were of AAS grade, purchased from E-Merck (certified purity > 99.99%). For the preparation of working standards, metal stock solutions (1000 ppm) were employed. Using standard reference materials provided by National Institute of Health, Islamabad, Pakistan, the accuracy of the method was evaluated by conducting inter laboratory comparison of the data. The two results were found to be in good agreement with ± 2.0 % for triplicate runs of the ash samples. STATISTICA software (StatSoft Inc. 1999) was used for statistical analysis of data.

Table 1. Information on samples codes and make of Pakistani cigarettes.

S. No.	Sample Code	Description
1.	PA-1	Capstan, King size
2.	PA-2	Cash, King size filter
3.	PA-3	Diplomat, King size filter
4.	PA-4	Embassy Kings
5.	PA-5	John Player Gold Leaf
6.	PA-6	Gold Street International, micron filter
7.	PA-7	Gold Flake, Wills, King size filter
8.	PA-8	K-2, King size filter
9.	PA-9	Morven Gold, King size Virginia
10.	PA-10	Princeton, luxury length
11.	PA-11	Press, filter cigarettes
12.	PA-12	Red and White, King size filter
13.	PA-13	Royals, filter cigarettes
14.	PA-14	Tanders, Virginia
15.	PA-15	Wills Kings

Table 2. Information on samples codes and make of foreign cigarettes.

S. No.	Sample Code	Description
1.	FA-1	Benson and Hedges, special filter (UK)
2.	FA-2	Business Club, Virginia blend, King size filter(UK)
3.	FA-3	Captain Black, filters, little cigars (USA)
4.	FA-4	Cartier, Vendome, lights, pearl tipped (UK)
5.	FA-5	Camel (USA)
6.	FA-6	Dunhill, International, filter deluxe (UK)
7.	FA-7	Davidoff (Germany)
8.	FA-8	Knights Bridge (Germany)
9.	FA-9	London, King size filter (UK)
10.	FA-10	Marlboro, filter class A cigarettes (USA)
11.	FA-11	Mild 88 (Korea)
12.	FA-12	More, menthol filter class A cigarettes (USA)
13.	FA-13	Rothman's Lights (UK)
14.	FA-14	Seven Stars, charcoal filter cigarettes (Japan)
15.	FA-15	555, filter kings (UK)

RESULTS AND DISCUSSION

All measurements were made using standard analytical conditions listed in Table 3. The heavy elements (Ni, Cr, Zn, Cd, Pb and Cu) determined at trace level in the ash of the cigarettes of both Pakistani and foreign origin, showed a wide variation with regards to concentration levels. This is expressed as $\overline{X}\pm SD$ in Table 4 and 5. Figure 1 and 2 indicate the extreme ranges of metal concentration in the ash of various versions of cigarettes. Changes in the composition of ash from cigarettes of various brands are associated with peculiarity of tobacco plant varieties and tobacco processing. Nickel was found to have divergent concentration values in the ash of local brands of cigarettes. Here maximum Ni concentration was found to be 5 μg/cig. in PA-6 whereas a minimum concentration of 1.0 μg/cig. was obtained for PA-4. In case of foreign brands, the situation was quite spurious because a concentration of 7 μg/cig. was encountered in as many as four brands FA-3, FA-4, FA-13 and FA-14. The lowest Ni concentration in this category was 0.4 μg/cig. for FA-15.

Table 3. Standard analytical conditions for atomic absorption analyses.

Element	λ (nm)	Flame	Detection Limit (ppm)
Cd	228.8	Air-C_2H_2	0.02
Cr	357.9	Air-C_2H_2	0.09
Cu	324.8	Air-C_2H_2	0.09
Ni	232.0	Air-C_2H_2	0.10
Pb	217.0	Air-C_2H_2	0.20
Zn	213.9	Air-C_2H_2	0.02

The case of Cr was found to be uniquely different compared with other metals as certain elevated levels were observed. For instance, the concentration of Cr in the ash of local brands of cigarettes is as high as 22 μg/cig. for PA-13; on the minimum side only PA-6 showed marginal concentration of the metal at 1.0 μg/cig., thus giving the 22-fold ash enhancement ratio between the extreme values of the metal concentration in the ash of cigarettes. This analysis clearly provides evidence as to the deleterious role of the metal towards human consumption. The Cr levels in the ash of foreign brands are again very divergent, spanning between 39 μg/cig. (FA-8 and FA-13) to 66 μg/cig. (FA-1).

Zn concentration levels in the ash of local brands showed a very wide ratio between the maximum and minimum metal concentrations. It is 72 μg/cig. for PA-5 and 0.1 μg/cig. for PA-11 depicting 72-fold enhancement ratio. But in the case of foreign brands, the difference is not as vast as maximum concentration level of 59 μg/cig. and minimum concentration level of 16 μg/cig. is obtained for FA-3 and FA-4 respectively, making a small ratio between extremum values. On the whole, the foreign brands are only slightly cleaner with respect to the Zn contents in relation to the counter parts from the local market.

The case of Cd distribution was, however, not so different from that of Ni. The samples PA-1, PA-2 and PA-8 exhibited the lowest concentration (1.0 μg/cig.) of the metal while the maximum concentration was 3 μg/cig. for samples PA-4 and PA-11, giving a 3-fold dispersion between the extreme concentration of Cd in the ash of local brands. The distribution of Cd in local brands is much more restricted

Table 4. Trace elements concentration level in ash of different Pakistani brands of cigarettes.

Trace Elements	Concentration $\overline{X} \pm$ S.D. (μg / cig.)														
	PA-1	PA-2	PA-3	PA-4	PA-5	PA-6	PA-7	PA-8	PA-9	PA-10	PA-11	PA-12	PA-13	PA-14	PA-15
Ni	3±0.2	2±0.1	1±0.1	0.1±ND*	1±0.1	5±0.2	1±0.1	3±0.2	4±0.2	3±0.2	2±0.1	1±0.1	1±0.1	0.3±0.2	2±0.1
Cr	15±0.3	16±0.4	20±0.3	14±0.3	9±0.3	1±0.1	3±0.2	7±0.3	6±0.3	2±0.1	21±0.4	5±0.3	22±0.4	6±0.2	14±0.3
Zn	14±0.3	13±0.3	20±0.3	41±0.4	72±0.5	18±0.3	10±0.2	16±0.4	19±0.3	2±0.2	0.1±0.1	0.3±0.1	0.3±0.1	2±0.2	1±0.1
Cd	1±0.1	1±0.1	2±0.2	3±0.2	2±0.1	2±0.1	2±0.1	1±0.1	2±0.1	2±0.1	3±0.2	2±0.1	2±0.1	2±0.1	2±0.1
Pb	1±0.1	15±0.3	17±0.4	28±0.3	27±0.4	16±0.3	10±0.2	12±0.2	22±0.2	19±0.3	22±0.2	23±0.3	15±0.2	22±0.2	18±0.2
Cu	14±0.3	13±0.2	19±0.2	10±0.2	11±0.2	1±0.2	9±0.2	13±0.2	12±0.2	13±0.2	9±0.2	10±0.2	12±0.2	16±0.3	9±0.2

*ND = Not Detected

Table 5. Trace elements concentration level in ash of different foreign brands of cigarettes.

Trace Elements	Concentration $\overline{X} \pm$ S.D. (μg / cig.)														
	FA-1	FA-2	FA-3	FA-4	FA-5	FA-6	FA-7	FA-8	FA-9	FA-10	FA-11	FA-12	FA-13	FA-14	FA-15
Ni	4±0.2	5±0.2	7±0.3	7±0.3	5±0.3	1±0.1	1±0.1	3±0.2	2±0.1	1±0.1	2±0.1	1±0.1	7±0.3	7±0.3	0.4±0.1
Cr	66±0.5	54±0.5	47±0.4	47±0.5	49±0.4	44±0.5	48±0.4	39±0.4	51±0.5	55±0.5	55±0.5	41±0.5	39±0.4	50±0.5	41±0.5
Zn	24±0.2	49±0.4	59±0.5	16±0.3	43±0.4	20±0.3	19±0.3	27±0.3	19±0.3	24±0.2	33±0.3	25±0.3	23±0.3	18±0.3	17±0.3
Cd	2±0.1	2±0.1	1±0.1	2±0.2	1±0.1	1±0.1	2±0.2	1±0.1	2±0.1	2±0.1	2±0.1	2±0.2	2±0.1	2±0.2	2±0.1
Pb	34±0.3	30±0.3	27±0.3	38±0.4	40±0.4	26±0.3	27±0.3	35±0.3	43±0.4	35±0.3	40±0.4	39±0.3	37±0.3	43±0.4	31±0.4
Cu	9±0.2	19±0.2	37±0.3	11±0.1	10±0.1	17±0.2	10±0.1	19±0.2	23±0.2	11±0.1	8±0.1	11±0.1	48±0.3	11±0.1	12±0.2

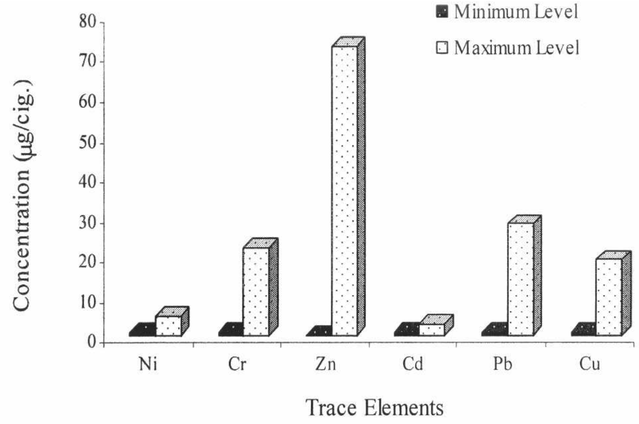

Figure 1. Extreme ranges of metal concentrations levels in ash of Pakistani brands of cigarettes.

than that of Ni. The maximum Cd concentration in the foreign brands is rated at 2 µg/cig. for FA-1, FA-2, FA-9, FA-10, FA-11, FA-13 and FA-15, and the minimum at 1.0 µg/cig. for FA-3, FA-5, FA-6 and FA-8.

The case of Pb is unique in the sense that its level both in the local and foreign brands is not very much divergent. The highest concentration of Pb in the ash of local brands of cigrarettes obtained was 28 µg/cig. for PA-4 and the lowest level obtained was 1.0 µg/cig. for PA-1, giving 28-fold enhancement ration. Although the concentration levels of Pb in the foreign brands of cigarettes were higher but not much variation in the extreme concentration levels existed between 43 µg/cig. (FA-9 and FA-14) and 26 µg/cig. (FA-6). Lastly, Cu concentration in the local brands varied between 1 µg/cig. to 19 µg/cig. for PA-6 and PA-3 respectively.

Table 6 and 7 list the correlation coefficient values for ash of local and foreign cigarettes, respectively. The linear correlation study was embarked with the objective to explore the possible correlation between pairs of metals in the ash of local and foreign cigarettes. The correlation statistics reveal a positive correlation for Pb and Cd at $r = 0.694$ in the ash of local brands of cigarettes. The picture on the foreign brands presented a different aspect of correlation. Only Ni is positively correlated with Cu ($r = 0.466$). This correlation study indicates a clear difference between the ash contents of cigarettes of both local and foreign brands.

A major concern out of this situation is the tolerance of these metals from the viewpoint of allowed limits of safe ingestion imposed by WHO. The present work revealed that consumption of cigarette could cause air quality contamination through resulting ash, thus enhancing trace metal levels in human body which causes adverse health effects for the consumers. Government should make efforts at discouraging continual consumption of these cigarettes but the public must also learn about the dangers of toxic metals and how to avoid them.

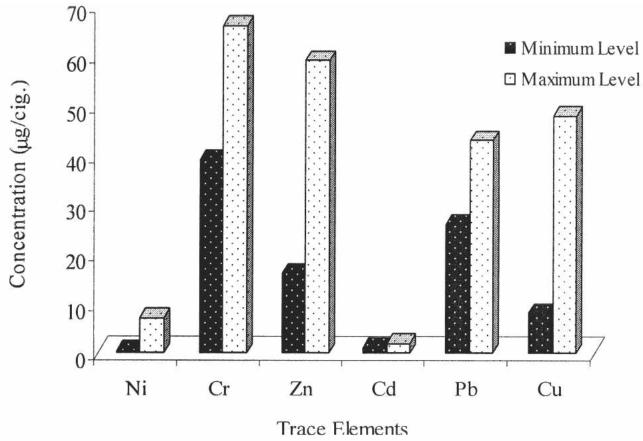

Figure 2. Extreme ranges of metal concentrations levels in ash of foreign brands of cigarettes.

Table 6. Correlation coefficient values for pairs of metals in ash of cigarettes of Pakistani origin.

	Ni	Cd	Cr	Zn	Pb	Cu
Ni	–	– 0.338	– 0.360	– 0.134	– 0.354	0.112
Cd		–	0.131	0.083	0.694*	– 0.373
Cr			–	– 0.052	– 0.065	0.061
Zn				–	0.366	– 0.008
Pb					–	– 0.232
Cu						–

* = Correlation is significant at 0.01 level

Table 7. Correlation coefficient values for pairs of metals in ash of cigarettes of foreign origin.

	Ni	Cd	Cr	Zn	Pb	Cu
Ni	–	– 0.107	0.034	0.360	0.205	0.466
Cd		–	0.312	– 0.463	0.327	– 0.202
Cr			–	0.149	0.094	– 0.405
Zn				–	– 0.264	0.305
Pb					–	– 0.160
Cu						–

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