

Distribution of Cadmium and Nickel of Tobacco During Cigarette Smoking

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■ Analyses of wet- and dry-ashed cigarettes, cigars, and pipe tobacco revealed that these products contained appreciable amounts of cadmium and nickel. Our results indicate values of 1.56–1.96 μg Cd and 4.25–7.55 μg Ni per cigarette, and 0.93–1.86 μg Cd/gram of cigar and pipe tobacco. Only 7–10% of the Cd and 0.4–2.4% of the Ni in the smoked portion of the cigarettes appeared in the particulate phase of the mainstream smoke (tsc); the remainder is present in the ash, trapped in the butt or lost in the sidestream. These data suggest that 38–50% of the Cd and 11–33% of the Ni in the smoked portion of cigarettes are present in the sidestream. Thus Cd and Ni in the sidestream smoke of cigarettes may present a health hazard to nonsmokers as well as smokers.

Cadmium and nickel are toxic metals which are present in our environment because of certain industrial uses and because of their widespread occurrence in foods, fuels, and many industrial products (Stokinger, 1963; Mastromatteo, 1967; Smith et al., 1960; Schroeder et al., 1961).

Several investigators (Nandi et al., 1969; Szadkowski et al., 1969) have attempted to assess the fate of heavy metals including cadmium during the smoking of cigarettes. Nandi et al. (1969) assumed that 69% of the cadmium in the unsmoked cigarette entered the mainstream. However, Szadkowski et al. (1969) reported that only 13% of the cadmium in the unsmoked cigarette was found in the inhalable mainstream smoke.

To delineate the cadmium and nickel distribution during smoking of nonfilter cigarettes in a more exact manner, we re-investigated this problem with the particular intent of confirming suspicions that the sidestream smoke might contain significant amounts of these trace metals, which could be detrimental to the health of the smoker as well as the nonsmoker.

Materials and Methods. Tobacco products: Reference cigarettes (KR) prepared for research purposes by the University of Kentucky Institute for Research on Tobacco were used in the main part of our study, and were from one lot. A popular commercial brand (CB), purchased on the market, consisting of two different lots was also tested for comparisons. All cigarettes were of the nonfilter type, measuring 85 mm in length, and weighing about 1.12 grams each.

For comparison, we determined the metal content of one brand of cigar and one brand of pipe tobacco, which were purchased on the market.

Smoking Procedure. Cigarettes were smoked on a Mason Mark III, 24-port smoker which was adjusted to provide a 35-ml puff in a 2-sec interval during each minute of smoking per cigarette. During the nonsmoking interval, the mouthpiece was exposed to the air. The cigarettes were smoked to a 23-mm butt (73% of total length).

The ash from the cigarettes used in each experiment was collected directly in metal-free beakers utilized for the wet-ashing procedure. Tobacco smoke condensate (tsc), which is the particulate phase of the mainstream smoke, was collected in cold acetone traps as previously described (Michael et al., 1971). The acetone was removed by evaporation at reduced pressure and the residue was ashed as described below. The butts remaining after the cigarettes had been smoked to the prescribed length were extinguished with deionized water and analyzed as indicated below.

Preparation of Analytical Samples. The samples of tobacco, ash, or tsc were either wet ashed or dry ashed. The two methods were used as convenience dictated, since no evident difference in results could be associated with these procedures. Wet ashing of smoked or nonsmoked tobacco products was accomplished by heating these materials with concentrated HNO_3 until liquefaction and oxidation occurred. The resultant solutions and reagent blanks were reduced by evaporation to approximately 1 ml prior to dilution with hot 10% HNO_3 for analysis.

Dry ashing was accomplished in a muffle furnace at 400–450°C after moistening the sample with concentrated nitric acid. The residue from the dry-ashing procedure was dissolved in 2 ml of concentrated HNO_3 , which was evaporated and the residue taken up in hot 10% HNO_3 for analysis.

Analytical Determinations. Analyses for cadmium, nickel, zinc, and lead by atomic absorption spectroscopy were made on the 10% nitric acid solution of the digested or ashed samples by aspirating these directly into a Perkin-Elmer Model 303 unit equipped with a Boling burner and recorder readout.

Values for each metal were determined by comparison with standard absorption curves using certified Fisher standards. It was found that recovery of added standard solution to samples was 92% for cadmium, 95% for nickel, 95% for zinc, and 98% for lead, using external standards.

Results

Metal Content of Tobacco Products. The cadmium, nickel, and zinc contents of several tobacco products are listed in Table I. The standard deviations for cadmium, nickel, and zinc mostly reflect the variability of metal levels in the samples and in different batches of the cigarettes.

The data show that cadmium occurs in all of the tobacco products at 1–2 $\mu\text{g/g}$ levels. Nickel was determined in KR and CB cigarettes only, giving 4.5 and 7.5 $\mu\text{g/cigarette}$, respectively.

The values for nickel in KR and CB cigarettes were two and

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Table I. Metal Content of Tobacco Products

Sample	Metal concn, ^a μg		
	Cd	Ni	Zn
Kentucky reference ^b cigarettes (KR)	1.56 \pm 0.19/cig (6) ^c	4.25 \pm 0.18/cig (2)	33.4 \pm 2.4/cig (7)
Commercial brand ^b cigarettes (CB)			
Batch 1	1.90 \pm 0.14/cig (4)	...	38.9 \pm 9.0/cig (4)
Batch 2	1.96 \pm 0.11/cig (4)	7.55 \pm 0.50/cig (4)	20.0 \pm 0.8/cig (4)
Cigar (commercial)	1.86/g	...	51.4/g
Pipe tobacco (commercial)	0.93/g	...	33.0/g

^a Values are mean \pm S.D.
^b KR cigarettes weighed 1.12 \pm 0.04 grams and CB cigarettes weighed 1.12 \pm 0.10 grams.
^c Digit in parentheses denotes number of samples.

three times as large, respectively, as that reported for German cigarettes (Szadkowski et al., 1969).

The zinc determinations in Table I, in conjunction with those in Table II, served as an analytical control. All types of tobacco products show high concentrations of zinc (Cogbill and Hobbs, 1957; Nadkarni and Ehmann, 1969, 1970; Nadkarni et al., 1970), ranging from 20 μg /cigarette in CB to 51.4 μg /g in a cigar.

Metal Content of Smoked Cigarettes. The metal contents of the smoked portion of cigarettes are listed in Table II. These include determined values for ash, tsc, and smoked butt, and calculated values for the smoked portion, and the sidestream. The sidestream Cd, Ni, and Zn were calculated as that part of the smoked portion which could not be accounted for by summing up the levels of each metal in the ash, tsc, and smoked butt.

The sidestream percentages in Table II are given in terms of the amount of cadmium, nickel, and zinc originally in the smoked portion of a cigarette.

CADMIUM. The results show that only a small percentage (10.1 and 7.0%) of the cadmium in the smoked portion of either the KR or CB cigarettes appears in the tsc and so would be directly available for pulmonary absorption by the smoker (Lewis et al., 1972). The amount of cadmium in tsc per cigarette is 0.12 and 0.10 μg for KR and CB cigarettes respectively, or about 2.4 and 2.0 μg per pack of 20 cigarettes. This amount is less than the amount in mainstream smoke found by Szadkowski et al. (1969). Nevertheless, depending on the chemical form of the cadmium, it may be a source of cadmium as well as a health hazard to the smoker (Schroeder et al., 1961; Lewis et al., 1972).

The total mainstream smoke consists of the tsc and what is trapped by the tobacco in the butt during smoking, designated butt enrichment. Thus the total mainstream cadmium of KR and CB cigarettes is 22 and 17%, respectively. The ash and mainstream cadmium constitute the readily measurable amounts, and in both types of cigarettes these sums are only 62 and 50% of the cadmium in the smoked portion. Thus, there remain 38 and 50% of original smoked portion cadmium to be accounted for.

This cadmium has been assumed as being present in the sidestream smoke—i.e., the smoke which drifts off the burning end of a cigarette between puffs. A preliminary result obtained in our laboratory (Hoegg et al., 1972) on directly collected sidestream smoke has indicated the presence of cadmium in an amount which was similar to the calculated values given here (0.43 and 0.72 μg cadmium per KR and CB cigarette, respectively); this is taken to be indicative of the logic of our method of estimating sidestream Cd. These amounts are equal to 8.6 and 14.4 μg for a pack of 20 KR and CB cigarettes, respectively.

The importance of the sidestream cadmium is that it represents a large amount of this toxic metal which is available for inhalation by both the smoker (Lewis et al., 1972) and anyone in his vicinity. It thus becomes a possible general indoor air contaminant.

NICKEL. Nickel has recently become a toxic metal of concern to environmental scientists. The data in Tables I and II show that it is present in considerable amounts in cigarettes, and like cadmium, a large portion is lost during smoking presumably as part of the sidestream smoke. The apparent loss of Ni during smoking of the KR and CB cigarettes (computed by subtracting the sum of Ni in tsc, ash, and butt from the total Ni in the whole cigarette) amounted to 1.03 μg per KR and 0.62 μg per CB cigarette. Thus, quantities of nickel, equivalent to 33% (KR) and 11% (CB) of the initial amount present in the smoked portion, were unaccounted for and are

Table II. Trace Metal Content of Cigarette Fractions

Fraction	Metal content ^a		
	Cd	Ni	Zn
KR cigarettes			
Smoked portion (73% of total)	1.14	3.10	24.3
Smoked butt	0.56 \pm 0.03 (6)	1.33 \pm 0.07 (2)	12.4 \pm 1.9 (6)
tsc ^b (mainstream particulate phase)	0.12 \pm 0.03 (5)	0.08	0.36
Ash ^b	10.1%	2.6%	1.5%
Sidestream ^{b,c}	0.45 \pm 0.03 (4)	1.81 \pm 0.16 (2)	21.3 \pm 4.7 (5)
	39.4%	58.4%	87.6%
	0.43	1.03	-0.66
	38%	33%	3%
CB cigarettes			
Smoked portion (73%)	1.43	5.51	14.6
Smoked butt	0.67 \pm 0.02 (4)	2.64 \pm 0.17 (4)	7.6 \pm 0.8 (4)
tsc ^b (mainstream particulate phase)	0.10 \pm 0.01 (2)	0.02 \pm 0.01 (2)	0.06 \pm 0.01 (2)
Ash ^b	7%	0.4%	0.4%
Sidestream ^{b,c}	0.48 \pm 0.02 (4)	4.27 \pm 0.20 (4)	11.9 \pm 0.5 (4)
	33.5%	77.5%	81.5%
	0.72	0.62	0.40
	50%	11%	3%

^a Concentrations are in μg per fraction listed. Values are means \pm S.D. or calculated values. Parentheses indicate the number of samples.
^b Percentages were calculated on basis of smoked portion.

^c Sidestream was calculated by subtracting the values of smoked butt, tsc, and ash from the total cigarette value given in Table I. (Butt enrichment can be estimated by subtracting the calculated value for unsmoked butt from the experimental value given.)

assumed to have entered the sidestream smoke. This results in 20.6 $\mu\text{g}/\text{pack}$ of KR and 12.4 $\mu\text{g}/\text{pack}$ of CB cigarettes, which is lost to the atmospheric environment of the smoker. The TSC nickel levels were 0.08 and 0.02 μg per KR and CB cigarettes respectively, indicating that only a very small amount of this metal is directly inhaled by the smoker.

ZINC. The data for zinc were obtained as a control on the analytical procedures, since its presence in the sidestream smoke was not expected to be significant. The values for zinc given in Table II show that 87.6 and 81.5% of the zinc in the smoked portions of KR and CB cigarettes respectively were found in the ash. The remainder of the zinc was mainly found in the mainstream smoke absorbed by the butt. Very little zinc was found in TSC and probably none was actually present in the sidestream. Thus, the fate of zinc is quite different from that of cadmium and nickel, a difference which emphasizes the importance of these metals in sidestream smoke.

LEAD. Untabulated values obtained for lead show a fate similar to that for zinc. Most of the lead was found in the ash and only 1.8–1.9% of the initial smoked portion was found in the TSC. It appears unlikely that the sidestream contained an appreciable amount of lead.

Discussion

These results not only lend support to the suggestion of Schroeder et al. (1961) and Lewis et al. (1972) that cadmium in tobacco represents a contributory source to the total body burden of the smoker, but also indicate that the presence of cadmium and nickel in the sidestream smoke may affect the health of both the smoker and anyone breathing the air in the general vicinity of the smoker.

From our data, it appears that 38–50% of the cadmium and 11–33% of the nickel of the smoked portion of cigarettes was released into the sidestream smoke. The TSC data suggest that a pack of 20 cigarettes would provide about 2 μg of cadmium and from 0.4 to 1.6 μg of nickel in the TSC which is inhaled by the smoker; the sidestream smoke, on the other hand, would put into the general environment 8.6–12.8 μg of Cd and 12.4–20.6 μg of nickel per pack. These amounts of Cd and Ni constitute a considerably greater environmental contamination than is found in ambient air. Although the smoker is the most exposed individual to the smoke, nevertheless, it could

be a hazard also to the nonsmoker in the vicinity of the smoker.

In addition, since there is considerable sidestream smoke derived from the smoking of cigars and pipe tobacco, the presence of cadmium in both of these products suggests that such sidestream smoke could also contain cadmium.

Since both cadmium and nickel are known to be harmful in occupational situations (Szadkowski et al., 1969; Friberg, 1957; Smith et al., 1960; Mastromatteo, 1967; Stokinger, 1963), and since smoking exposes a very large number of people to these toxic metals, the presence of cadmium and nickel in tobacco products (especially cigarettes) needs to be carefully considered in evaluating the health effects of tobacco smoking (Anderson et al., 1964; Lewis et al., 1972).

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