

CADMIUM AND LEAD IN CIGARETTES AND IN SMOKE CONDENSATE

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The cigarettes of three commercial brands (belonging to JUS quality classes E, II and IV) were analysed for cadmium and lead in tobacco, butts and crude smoke condensate. Metal fractions transferred from the cigarette tobacco to the smoke as well as metal retentions in the butts were calculated from the analytical results. Statistical analyses revealed a significant dependence of all observables on the cigarette quality class.

Cigarette smoking undoubtedly contributes a non-negligible fraction to man's overall intake of hazardous heavy metals such as cadmium and lead (1). Several groups have reported the analytical data on cadmium content in cigarettes, snuff and tobacco leaves, as well as in the cigarette smoke condensate (2..9). The data on lead and other trace metals are less numerous (5, 7, 10).

In the present paper the determinations of cadmium and lead content in three commercial brands of Yugoslav cigarettes, in their smoke condensates and butts are described. The aim of the study was to relate these observables, as well as the quantities derived from them (tobacco-to-smoke metal transfer fraction, butt retention) to the cigarette quality class and kind of metal. The final analytical determinations were done by differential pulse anodic stripping voltammetry (DPASV), a method which — to the best of the authors' knowledge — has not yet been applied in the studies of trace metals in tobacco products. Therefore, the analytical data reported here are an additional, independent support to the values determined by other workers.

EXPERIMENTAL

Sample

Cigarettes of three different brands (belonging to JUS* quality classes Extra, II and IV — the last one without filter tip), 100 per brand, were bought in the summer of 1984 in several tobacco shops throughout the city of Zagreb. Samples (containing four cigarettes each) were formed in a random way from each brand. The samples were then analysed for lead and cadmium content in tobacco, paper, filter tips, butts and crude smoke condensate. The average total mass (\pm std. dev.) of the cigarettes was as follows: E, (1.021 ± 0.053) g; II, (1.017 ± 0.084) g; IV, (0.976 ± 0.087) g.

Chemicals

All chemicals were of Merck »Suprapur« brand. The water was first de-ionised and then twice distilled in an all-glass still. The metal stock solutions, containing 1 g/L of lead or cadmium, were acidified with nitric acid (0.1 mmol/L) and standardised complexometrically. Mass concentrations of metals in working standard solutions, which were prepared daily, were in the range of $(0.1 \dots 1) \mu\text{g/mL}$.

Smoke condensate

Twenty cigarettes from each brand were smoked by means of H. Borgwaldt (Model RM 20/68) smoking machine in order to obtain the total particulate matter in the mainstream smoke which was later analysed for lead and cadmium. The condensate was trapped electrostatically onto a glass test tube and dissolved in 30 mL of methanol. The crude condensate weighed 530.7 mg, 440.8 mg and 661.5 mg for quality classes E, II and IV, respectively. The smoking programme followed closely CO-RESTA standard method No. 10 (11): puff volume 35 mL, puff duration (2.0 ± 0.2) s, puff frequency $1 \text{ min}^{-1} = (1/60) \text{ s}^{-1}$. On the average, class E cigarettes needed 9.6 puffs to leave a butt 28 mm long, class II being similar (10.3 puffs per cigarette, for the same butt length), while for class IV cigarettes these figures were 13 puffs, 23 mm.

Digestion procedures

All samples were mineralised by a wet method, using Tecator DS-40 Digestion System, consisting of a programming unit (up to 9 program steps in a run), heating block (accommodating up to 40 digestion tubes), and a vacuum exhaust. The following mixture of concentrated acids was used for mineralisation: HNO_3 (60 mL), HClO_4 (38 mL), H_2SO_4 (2 mL).

The samples of cigarette tobacco, paper, filter tips and butts were weighed, transferred into the digestion tubes and then 5 mL of acid mix-

* Yugoslav industrial standards

ture was added. The digestion program was: 50 °C (3 h), 100 °C (5 h), 150 °C (8 h), 200 °C (8 h), 230 °C (8 h). After digestion a white residue was obtained which was dissolved in 20 mL of HCl solution (0.05 mol/L). The residues resulting from the ashing of tobacco samples were not completely soluble in dilute HCl, therefore the tubes were first vigorously shaken in order to extract as much metal as possible and then left until the insoluble residue settled. The aliquots for analysis were carefully drawn with a pipette. There were no difficulties with dissolving the ashing residues of either of the remaining samples (paper, filter tips, butts, condensate).

Condensate samples were processed in a slightly different way. The procedure had to start with evaporating methanol (60 °C, 3 h) in order to obtain a brown residue which was then subjected to the same procedure as described above.

Voltammetric analyses

Lead and cadmium contents in all samples were determined by differential pulse anodic stripping voltammetry (DPASV) on a hanging mercury drop electrode (HMDE). The apparatus used was a Model 374 Polarographic Analyzer (Princeton Applied Research Co.) equipped with a Model 303 Static Mercury Drop Electrode.

Analytical parameters:

- electrode: HMDE, medium size
- technique: DPASV
- mode: blank
- initial voltage (vs. Ag/AgCl): -0.75 V
- final voltage (vs. Ag/AgCl): -0.25 V
- deposition time: 300 s
- equilibration time: 15 s
- scan rate: fast
- sensitivity: medium
- peak locations (approx.) -0.600 V (Cd), -0.410 V (Pb)

A 50 mmol/L aqueous HCl solution was used as the supporting electrolyte. The concentrations were determined by the standard addition method: three standard additions were made for each sample and the results were evaluated by linear regression. The criterion for the internal consistency of a standard addition run was the magnitude of the squared correlation coefficient: $r^2 \geq 0.99$ (12).

Reagent blanks were recorded and evaluated wherever appropriate. Automatic blank-curve subtraction facility was not used because of a rather low level of nonspecific signal at the voltages of interest.

RESULTS

The metal contents in cigarette tobacco, butts and the smoke condensate for the three cigarette brands examined are shown in Table 1, expressed in micrograms per one cigarette, as are their standard deviations and ranges. All figures were rounded to the first significant digit in the standard deviation.

Table 1
Cadmium and lead content in cigarettes belonging to three quality classes (expressed per one cigarette)

Quality class	Sample	Metal	Mean \pm S.D. μg	No. of replicates	Range μg
Extra	Tobacco	Cd	2.5 ± 0.6	17	1.50 .. 3.20
		Pb	1.1 ± 0.3	17	0.63 .. 1.75
	Butt	Cd	0.5 ± 0.1	19	0.35 .. 0.57
		Pb	0.5 ± 0.1	19	0.34 .. 0.66
	Condensate	Cd	0.22 ± 0.01	5	0.21 .. 0.22
		Pb	0.10 ± 0.01	5	0.09 .. 0.11
II	Tobacco	Cd	2.6 ± 0.6	17	1.34 .. 3.54
		Pb	1.5 ± 0.3	16	0.92 .. 2.11
	Butt	Cd	0.6 ± 0.2	20	0.27 .. 0.80
		Pb	0.8 ± 0.2	20	0.36 .. 1.00
	Condensate	Cd	0.24 ± 0.02	5	0.22 .. 0.26
		Pb	0.10 ± 0.02	5	0.08 .. 0.11
IV	Tobacco	Cd	2.6 ± 0.9	19	1.08 .. 4.33
		Pb	2.1 ± 0.6	18	1.21 .. 3.40
	Butt	Cd	1.1 ± 0.3	18	0.52 .. 1.58
		Pb	0.9 ± 0.3	18	0.35 .. 1.31
	Condensate	Cd	0.27 ± 0.02	5	0.25 .. 0.29
		Pb	0.15 ± 0.01	5	0.13 .. 0.17

The metal contents of the cigarette paper and filter tips were well inside the variability of the tobacco, butt and condensate results and were therefore considered negligible.

The values of metal transfer fractions (tobacco \rightarrow smoke) and metal retentions in the butts were computed from the data shown in Table 1 and can be found in Tables 2 and 3, together with some statistical parameters. These quantities are defined by the formulae:

$$t = m_M(\text{cond.})/m_M(\text{tob.}) \quad (\text{transfer fraction})$$

$$R = m_M(\text{butt})/m_M(\text{tob.}) - r \quad (\text{butt retention})$$

$$r = \frac{l_{\text{cig.}} - l_{\text{tip}}}{l_{\text{butt}} - l_{\text{tip}}} \quad (\text{correction term to } R)$$

where m_M denotes mass of M (Cd or Pb) contained in one cigarette while (l) stands for length; abbreviations cig., cond. and tob. are self-explaining. The variances of t and R (r was considered a constant) were computed from the well-known formula for the variance, V , of a ratio of two uncorrelated variates (A and B , say) with known variances:

$$V(A/B) = B^{-4}(A^2V_B + B^2V_A).$$

Because the numerator and the denominator were both derived from many measurements (N_A and N_B , say) these can be combined to give $N_A N_B$ estimates of A/B . In the subsequent statistical analyses, however, only $(N_A - 1)$ ($N_B - 1$) degrees of freedom were assigned to such ratios.

Table 2

Transfer of metals from tobacco to smoke condensate: mean transfer fractions ($t_i^{(0)}$) \pm 95% confidence limits and one-way analyses of variance

Quality class	Cd	Pb
E	8.8 \pm 0.4	9.2 \pm 0.6
II	9.1 \pm 0.5	6.4 \pm 0.4
IV	10.2 \pm 0.8	7.0 \pm 0.4
$F_{\text{obs.}}$	12.207	49.748
$\varphi_1, \varphi_2^{\text{a)}}$	2; 186	2; 190
$P^{\text{b)}}$	<0.01	<0.01

a) No. of degrees of freedom for »between quality classes« and residual mean squares, respectively;

b) $P = P(F \geq F_{\text{obs.}} | \varphi_1, \varphi_2)$.

Table 3

Metal retention in the butts: mean retentions ($R_i^{(0)}$) \pm 95% confidence limits and one-way analyses of variance

Quality class	Cd	Pb
E	15.4 \pm 0.6	40.4 \pm 1.8
II	14.8 \pm 0.8	43.3 \pm 1.7
IV	12.5 \pm 2.0	12.4 \pm 2.0
$F_{\text{obs.}}$	5.545	1558.5
$\varphi_1, \varphi_2^{\text{a)}}$	2; 896	2; 860
$P^{\text{b)}}$	<0.01	<0.01

a) No. of degrees of freedom for »between quality classes« and residual mean squares, respectively;

b) $P = P(F \geq F_{\text{obs.}} | \varphi_1, \varphi_2)$.

DISCUSSION

From the data displayed in Table 1 the coefficients of variation can be easily computed: they fall in the range of 5..35%, thus indicating that the data variability is tolerably low. This gives a support, though not a proof, to the belief that a sufficiently large sample has been taken. By comparing these data to those collected by others (see references quoted in the Introduction) it is seen that the figures for cadmium agree very well; the values reported by Šorak-Pokrajac (9) are slightly higher but nevertheless fall in the ranges quoted in Table 1. The figures for lead determined by Marić-Tesarova and co-workers (10) are somewhat higher than those found in the present work but also fall in their overall range.

Table 4
Differences in metal content (expressed per one cigarette) between quality classes found in a one-way analysis of variance

Sample	Metal	$F_{\text{obs.}}^{\text{a)}$	$\varphi_1^{\text{b)}$	$\varphi_2^{\text{b)}$	$P^{\text{c)}$	Order ^{d)}
Tobacco	Cd	0.222	2	50	>0.1	$E \approx II \approx IV$
	Pb	27.547	2	48	<0.01	$E < II < IV$
Butt	Cd	46.944	2	54	<0.01	$E < II < IV$
	Pb	17.746	2	54	<0.01	$E < II < IV$
Condensate	Cd	18.347	2	12	<0.01	$E \approx II < IV$
	Pb	31.808	2	12	<0.01	$E < II < IV$

a) Observed variance ratio (variance between classes/residual variance);

b) Number of degrees of freedom of the above variances;

c) $P = P(F \geq F_{\text{obs.}} | \varphi_1, \varphi_2)$; F : Fisher's variance ratio;

d) Order of quality classes according to metal content, checked by Wilcoxon-Mann-Whitney test.

By simple one-way analysis of variance it was possible to show that there were significant differences in the content of either metal between three cigarette brands. The statistical evidence is reproduced in Table 4. By performing, in addition, Wilcoxon tests for location differences the order of cigarette brands with respect to metal content was established. It was found (with one exception) that the metal content in either tobacco, butts or condensate increased with decreasing quality. Because the significance levels in all the tests performed were rather high, this order seems to be reliably established.

Cadmium transfer fractions, reproduced in Table 2, are generally higher than most of those reported earlier, except the values determined by Šorak-Pokrajac (9) but the differences are not likely to be significant.

By applying one-way analysis of variance again, it can be shown that, for both metals, the transfer fraction also significantly depends on the quality class (see Table 2): for cadmium there is an increase in t with decreasing cigarette quality while no regularity is seen for lead. The results of simple one-way analysis were supported by a two-way factorial analysis of variance which indicated, at high significance level ($P < 0.01$), that the transfer fraction, t , can be regarded as being a resultant of two factors (kind of metal and quality class), with a considerable cross term («interaction»). It is interesting to note that cadmium transfer fraction is only slightly higher in Class IV cigarettes, which have no filter tips, than in the two remaining brands which are filter-tipped. The data for t_{Pb} are still more surprising. At present, it would be very hard to find an explanation for this.

The data for butt retention were analysed in a completely identical way (see Table 3). Here, a more logical pattern was observed: the metal retentions for two higher quality brands (filter-tipped) are clearly higher than those for the lowest quality one (no filter tip). There is a dramatical difference between R_{Cd} and R_{Pb} in Classes E and II.

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Sažetak

OLOVO I KADMIJ U CIGARETAMA I DIMNOM KONDENZATU

Metodom inverzne voltametrije na višećoj živinoj kapi (DPASV) određene su količine kadmija i olova u cigaretama triju vrsta (kvalitetni razredi prema JUS-u: Extra, II i IV). Pored duhana, papira i filtarskih čepića analizirani su i opušci i sirovi dimni kondenzat. Iz analitičkih rezultata izračunana je frakcija prijenosa metala iz duhana u dimni kondenzat kao i retencija metala u opušku. Statističkim analizama utvrđena je ovisnost svih opservabli o kvalitetnom razredu cigarete.

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