

DETERMINATION OF COPPER AND ZINC IN DIFFERENT BRANDS OF CIGARETTES IN JORDAN**Adnan Massadeh,^{a,*} Feras Alali,^a and Qasem Jaradat^b**^a*Department of Medicinal Chemistry and Pharmacognosy, Faculty of Pharmacy, Jordan University of Science and Technology, P.O. Box 3030, Irbid, Jordan,**E-mail: massadeh@just.edu.jo, Fax: 00962-2-7095019*^b*Chemistry department, Faculty of Science, Mutah University, Al-Karak, Jordan**Received 04-11-2002***Abstract**

Copper and Zinc were determined in cigarettes of freshly opened packs. Cu and Zn concentrations in different cigarette brands sold and/or produced in Jordan were determined by Atomic Absorption Spectrometry (AAS). The accuracy and precision of the method were tested with standard reference materials BCR-CRM 280 (rye grass) and NIST-SRM 1570a (spinach leaf). Average levels of Cu and Zn in cigarettes analysed were 12.90 and 55.62 $\mu\text{g g}^{-1}$ (DW), respectively. An average of 0.2% and 1.0% of Cu and Zn, respectively were estimated to pass to mainstream smoke. Our results are in good agreement with other studies in the worldwide.

Introduction

Copper is the third most abundant trace element in the body, following zinc and iron. There are a lot of disorders, which are associated with the toxic effects of copper accumulated in tissues such as the liver, brain, cornea and kidney or copper deficiency. These disorders include Wilson's disease, Menkes disorder and Indian Childhood Cirrhosis.^{1,2}

Cigarette smoke contains both organic and inorganic compounds that are human carcinogens. According to WHO, every 10 seconds another person dies as a result of tobacco use.³ With 4000 compounds identified in tobacco smoke, most Chemicals in cigarette smoke known to be harmful to man.^{4,5} Unlike Cd and Pb in cigarettes, little information on the concentrations of other elements, including Cu and Zn is available. It was reported that heavy metals such as Cu and Zn inhibit pollen germination and pollen tube growth in plants including tobacco plant, reaching toxic levels in the plant leaves and causing ultra-structural changes.⁶

Several heavy metals found in tobacco smoke, such as Cd, Cr, Pb and Ni, also accumulate in tissues and fluids in relation to smoking.⁷⁻¹⁰ Mussalo-Rauhamaa et al.¹¹ reported that the mean content in filter cigarette tobacco sampled from Finland was

15.6 $\mu\text{g g}^{-1}$ (DW) for Cu. Other researchers found the mean concentration of Cu in UK cigarettes and Korean cigarettes were 13 and $< 10 \mu\text{g g}^{-1}$ (DW), respectively.¹²

Zinc is required for many aspects of fetal growth and development.¹³ Authors documented that pregnant women who smoke have higher levels of Zn in the placenta and their infants have significantly lower levels of Zn in the red blood cells.¹⁴ Moreover, increased Zn levels in pregnant women in Cleveland, Ohio, USA as a result of smoking led to increased placental Zn levels, and decreased the cord vein red blood cell Zn levels in infants of smoker.¹⁴ Smoking during pregnancy results in a decrease in infant birth weight,¹⁵ due to hypoxia and vasoconstriction in the uterine vessels.¹⁶ Moreover, it was reported that there is a relationship between Cd, Zn and birth weight in pregnant women who smoke.¹⁵

Researchers reported that Cu and other metals were increased significantly in cataractous human lens due to cigarette smoking.¹⁷ Current smoking or number of cigarettes smoked per day might be a significant risk factor in cataractogenesis.

The consumption of tobacco products and the number of smokers have been increasing steadily throughout the world. Jordan, 5 million in population, imports and produces several tobacco cigarettes brands. Customers pay more than 283 million dollars yearly. Moreover, the area where tobacco has been grown in Jordan is about 30,000,000 m^2 of the best fertilize soils. The average annual consumption per person in Jordan is about 1680 cigarettes.¹⁸

The main aims of this research were to measure the Cu and Zn concentrations in different brands of tobacco cigarettes sold and/or produced in Jordan, to find if there are significant differences between cigarette brands in their Cu and Zn contents, to estimate the approximate amounts of these elements in the mainstream smoke according Mussalo-Rauhamaa et al. study,¹¹ and to compare our results with those in some other countries.

Experimental

Reagents and Glass Ware

Standard solutions at 1000 ppm of Cu and Zn, 35-38% HCl (Scharlau), and 70% HNO₃ (Scharlau) were used for preparation of samples and standards. Glassware were

soaked in 10% HNO₃ for 24 hours; cleaned with de-ionized water and dried to ensure that no contamination from glassware occur.

Instruments

A Varian (Spectra AA-10) flame atomic absorption spectrometer with computer system was employed throughout the experiments. The wavelengths employed for Cu and Zn were 324.7 and 213.9 nm, respectively, the slit width was set to 1 nm. The flow rate of acetylene was set to 1.5 ml/min. Air–Acetylene flame was used. A Sartorius analytical balance (A 120 S), shaker with water bath (D-3162 Kottermann labortechnik, type 3047, West Germany), PTFE vessel and oven (D4 C Genlab, Widnes, England) were employed in experiments.

Collection of Samples

Nineteen different brands of cigarettes were purchased from Jordan market. Composites were prepared by removing the papers and filters of 20 cigarettes taken randomly from four packs of 20 cigarettes, 5 cigarettes from each pack, of the same brand with different batch numbers, and mixed together. The weight for the 20 cigarettes ranged from 662-722 mg per cigarette.

Acid Digestion Method

The method described was used in this study for determination of Cu and Zn in cigarettes by atomic absorption spectrometry. A weight of 0.5 g of air–dried tobacco sample was placed in a PTFE vessel and allowed to digest with a mixture of HNO₃ and HCl (8:2 v/v) by heating the PTFE vessel on the water bath-shaker for 5 hr at 105 °C. After cooling 10 mL of de-ionized water was added, the solution was filtered through a Whatman filter paper (grade 1) into a 25 mL volumetric flask; and made to the mark with de-ionized water.¹¹ Quantitative analysis is achieved by preparing the relevant calibration curves from solutions of aqueous metal standards of the same acid concentration as samples to minimize matrix affects. This method was compared with Mussalo-Rauhamaa et al. procedure.¹¹

Results and Discussion

The results of Cu and Zn determination in tobacco materials using the acid digestion method, and the amounts of these metals passed into mainstream smoke are given in Tables 1 and 2, respectively.

Copper concentrations in Jordan market cigarettes averaged $12.90 \mu\text{g g}^{-1}$ (DW) with range of 11.37 to $14.42 \mu\text{g g}^{-1}$. This is comparable with reported results for Cu in UK ($13 \mu\text{g g}^{-1}$) and 1.7 times higher than reported results for Korean cigarettes ($7.73 \mu\text{g g}^{-1}$). The concentrations of Zn in Jordan cigarettes averaged $55.62 \mu\text{g g}^{-1}$ (DW) with range of 45.65 to $65.58 \mu\text{g g}^{-1}$. Compared with reported results for Zn in UK ($31.9 \mu\text{g g}^{-1}$) and Korea ($38.5 \mu\text{g g}^{-1}$),¹¹ the average Zn contents in Jordan cigarettes are higher 1.4 and 1.8 times, respectively.¹¹

Table 1. The weight (g) and concentration of Cu $\mu\text{g g}^{-1}$ (DW) and average estimated amount of Cu passed to mainstream smoke for one pack of 20 cigarettes-a day smoker in 19 different brands cigarettes in Jordanian market.

No.	Cigarette brands	Wt. of 20 Cigarettes(g)	Cu conc. $\mu\text{g g}^{-1}$ (DW)	Estimated amount of Cu in stream smoke (μg)
1	Rum light	13.94	16.60	0.46
2	Classic	14.80	12.00	0.35
3	Rothman	13.82	9.55	0.26
4	Kareem	14.12	14.65	0.41
5	NOVA	12.56	18.60	0.47
6	Mond light	13.77	10.90	0.30
7	Marlborow	12.82	10.70	0.27
8	Viceroy light	13.00	13.00	0.34
9	Winston light	12.51	13.10	0.33
10	Palace light	13.48	14.26	0.38
11	Palace	16.96	11.30	0.38
12	Marlborow light	13.18	11.25	0.30
13	Winston	13.66	11.20	0.31
14	Gold star	16.53	11.70	0.29
15	Viceroy	12.69	11.55	0.29
16	Kent light	12.44	10.55	0.26
17	Kent	15.00	21.60	0.25
18	Hamawi Momtaz	*13.84	10.90	0.30
19	Heishi	*13.84	15.62	0.43

* Weights of Hamawi momtaz and Hieshi tobacco are estimated, because they are unpacked unlike other types.

Table 2. The weight (g) and concentration of Zn $\mu\text{g g}^{-1}$ (DW) and average estimated amount of Zn passed to mainstream smoke for one pack of 20 cigarettes-a day smoker in 19 different brands cigarettes in Jordanian market.

No.	Cigarette brands	Wt. of 20 Cigarettes(g)	Zn conc. $\mu\text{g g}^{-1}$ (DW)	Estimated amount of Zn in stream smoke (μg)
1	Rum light	13.94	45.84	6.39
2	Classic	14.80	41.85	6.19
3	Rothman	13.82	73.90	10.21
4	Kareem	14.12	88.00	12.21
5	NOVA	12.56	59.80	7.51
6	Mond light	13.77	88.05	12.12
7	Marlborow	12.82	45.16	5.81
8	Viceroy light	13.00	62.35	8.11
9	Winston light	12.51	39.70	4.97
10	Palace light	13.48	46.18	6.10
11	Palace	16.96	47.65	8.08
12	Marlborow light	13.18	38.90	5.13
13	Winston	13.66	34.30	4.68
14	Gold star	16.53	107.30	17.74
15	Viceroy	12.69	48.60	6.17
16	Kent light	12.44	76.60	9.03
17	Kent	15.00	38.55	5.78
18	Hamawi Momtaz	*13.84	40.00	5.54
19	Heishi	*13.84	40.65	5.63

* Weights of Hamawi momtaz and Hieshi tobacco are estimated, because they are unpacked unlike other types.

Table 3. Results of analysis of two NIST and BCR standard reference materials.

Standard Reference Material	Element	Certified value $\mu\text{g g}^{-1}$	Acid digestion $\mu\text{g g}^{-1}$	Mussalo-Rauhamaa etal $\mu\text{g g}^{-1}$
BCR-CRM 281 (ryegrass)	Cu	9.65 ± 0.38	9.44 ± 0.11	9.49 ± 0.06
	Zn	31.5 ± 1.4	30.97 ± 1.30	31.03 ± 1.42
NIST-SRM 1570a (spinach leaf)	Cu	4.7 ± 0.24	4.33 ± 0.18	4.34 ± 0.13
	Zn	82 ± 3.28	80.44 ± 2.83	80.0 ± 2.58

Validation of Method and Results

To confirm the reliability of the proposed method for the analysis of Cu and Zn in cigarettes two certified reference materials BCR-CRM-281 (rye grass) and NIST-SRM 1570a (spinach leaf) were analyzed by the acid digestion method. The results obtained

are within the uncertainty range of the certified values for Cu and Zn as shown below in Table 3. Also, to check the accuracy, quality control (QC) samples were carried out during the analysis of each examined element, the results were in consistence with QC concentrations. The relative standard deviation values of repeated measurements were less than 5% for both Cu and Zn.

Statistical Analysis of the Data

The statistical analysis was performed with ANOVA, and Student's t test. Statistical differences were found between brands in the Cu and Zn contents in cigarettes. ANOVA analysis for Cu and Zn show that there are significant differences in their concentrations of the 19 different brands of cigarettes tested. For Cu, F calculated value is $379.843 > F$ critical value of 1.741 at degree of freedom of 18.

For Zn, F calculated value is $1541.81 > F$ critical value of 1.741 at degree of freedom of 18.

When two standard reference materials BCR-CRM 281 (rye grass) and NIST-SRM 1570a (spinach leaf) were analyzed by the acid digestion method used in this work and by Mussalo-Rauhamaa et al. procedure,¹¹ the results were comparable as no statistically significant difference using t-test were found between the two methods (see Table 3).

Conclusions

Cu and Zn concentrations in cigarettes vary with the brand of cigarettes. This study confirms that tobacco is a notable source of metal pollutants Cu and Zn. The average concentrations of Cu and Zn in Jordanian cigarettes were 12.90 and 55.62 $\mu\text{g g}^{-1}$ (DW) respectively.

An average of 0.2% of Cu and 1% of Zn contained in tobacco is assumed to pass into the mainstream smoke.¹¹ Thus, based on the results of this study an extra daily intake of 0.36 (0.31-0.40) μg of Cu and 7.76 (6.16-9.35) μg of Zn was estimated for an average smoker (20 cigarettes/day).

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Povzetek

Z atomsko absorpcijsko spektrometrijo smo določali koncentracijo bakra in cinka v različnih vrstah cigaret, ki se proizvajajo oziroma prodajajo v Jordaniji. Povprečna vsebnost bakra in cinka je bila 12.90 oziroma 55.62 $\mu\text{g g}^{-1}$.