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THE CHANGE OF VOLATILE PHENOLS CONTENT IN CIGARETTE SMOKE CONDENSATE BY THE ADDITION OF METAL SALTS TO CIGARETTES BEFORE SMOKING

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Abstract. *Phenolic compounds are very important constituents of cigarette smoke condensate (CSC) and they have a significant effect on the overall aroma, flavor, and biological properties of cigarette smoke. Many of them are toxic, and in this study we investigated the change of volatile phenols content in CSC by the addition of $CaCl_2$, $FeCl_2$, $FeCl_3$, and $CuCl_2$ to cigarettes before smoking. In some cases the phenols content in CSC was significantly reduced (up to 20%), as well as the mass of tar and CO content of mainstream cigarette smoke.*

Key words: *cigarette smoke condensate, phenols, metal salts*

1. INTRODUCTION

Cigarette smoke condensate (CSC) presents a very complex system which contains many compounds with the profound influence on the smokers senses thus largely contributing to the cigarette consumption. Very important components of CSC are some phenolic compounds which have a significant effect on the overall aroma, flavor, and biological properties of cigarette smoke [1-3]. By using chromatographic methods large number (well over 100) of different phenolic compounds have been identified as a products of tobacco pyrolysis [4]. Many of them are toxic, contributing mainly to the strong carcinogenic and/or cocarcinogenic effect of CSC [5]. The most abundant in CSC are phenol, cresols, dihydroxybenzenes, and various polysubstituted phenols [6-8], although simple phenols are only the minor constituents of cured tobacco leaf [1,2]. Their presence in tobacco smoke is mainly the consequence of the pyrolytic reactions of lignin,

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cellulose, and various phenolic plant pigments. The polyphenolic constituents of tobacco could be reduced by genetic and agronomic practices in order to decrease the phenolics content of cigarette smoke and thus yield a safer smoking product.

In this study we investigated another, to the authors knowledge new and original, approach for reducing phenolics content of cigarette smoke by influencing pyrolytic conversion of tobacco constituents into phenols with the addition of some inorganic metal salts to the cigarettes before smoking. For this purpose we choosed $CaCl_2$, $FeCl_2$, $FeCl_3$, and $CuCl_2$ because corresponding metal ions have different redox characteristics. All the metal salts used in this study were taken to be chlorides in order to be sure that different results are the effect of different metal ions and because chlorides are convenient due to their good solubility in water.

2. EXPERIMENTAL

Cigarettes used in this study have been manufactured by DIN Tobacco Factory, Niš, and they present commercial brands from two different quality groups, I and IV. Preparation of cigarettes and collection of CSC electrostatically precipitated in an automatic smoking machine (Heinr. Borgwaldt, RM 20/CS) was performed under standardized conditions [9].

Aqueous solutions of metal chlorides (10 g/L of metal ion) have been added to cigarettes after physical examination. A volume of 100 μL was injected by a microsyringe in order to obtain the concentration of 1mg of metal ion/cigarette. Injection was performed axially along the whole length of cigarettes as evenly as possible.

Total content of the steam-volatile phenols was determined spectrophotometrically employing the 4-aminoantipyrine method [10]. For the phenols analysis the electrostatically precipitated CSC of 10 cigarettes has been dissolved in 10% NaOH, and then the phenols were steam distilled from solution which has been acidified to pH 4 with 3.75M H_3PO_4. Phenol, as well as *ortho*- and *meta*- substituted phenols, react with 4-aminoantipyrine during the oxidation with $K_3[Fe(CN)_6]$ in alkaline media and give a stable colored compound well soluble in chloroform with an absorbance maximum at 456 nm. The calibration curve for quantitative analysis was established by using aqueous solutions of freshly distilled phenol. This method of phenols determination in CSC is very convenient for routine analysis since it is relatively simple, fairly reproductive, and sensitive. Furthermore, a good correlation has been shown between values for phenol content obtained by gas chromatography and volatile phenols content determined by the spectrophotometric 4-aminoantipyrine method [11].

Beside the phenols content of CSC, the mass of tar and carbon monoxide (CO) content of mainstream smoke have also been determined. The CO content was measured by an indirect method (after collection in polyethylene bags) employing an automatic gas analyzer (Heinr. Borgwaldt CO analyzer).

In order to estimate the relative error of measurements we performed three independent determinations of volatile phenols content, mass of tar, and CO content in cigarettes without addition of metal salts. Relative error was calculated by using simple formula:

$$\text{Relative erorr}\,(\%) = \pm\left(\frac{\text{max. value - min. value}}{\text{max . value + min. value}}\right)\times 100$$

and we obtained the relative error values of ±4.7%, ±1.6%, and ±5.2% for the phenols content, mass of tar, and CO content, respectively.

3. RESULTS AND DISCUSSION

The results obtained by the volatile phenols content determination in CSC of cigarettes of the I and IV quality group with and without addition of inorganic metal salts before smoking are shown in the following Table.

Table 1.

Quality group	Phenol content (μg/cigarette)				
	no addition	$CaCl_2$	$FeCl_2$	$FeCl_3$	$CuCl_2$
I	30.1	30.8	28.6	28.3	28.5
IV	50.7	50.5	47.6	44.3	41.1

As can be seen from the results in Table 1, addition of inorganic metal salts to cigarettes before smoking reduces the phenols content of CSC except in the case of $CaCl_2$. The addition of $CaCl_2$ practically had no effect on the phenols content of CSC. This is not surprising because the quantity of Ca(II) ion added to cigarettes before smoking (1mg/cigarette) is far below the background level of calcium, which is in fact the most abundant metal in cured tobacco (about 27.5mg/g mainly in the form of organic acid salts) [2]. For comparison the background levels of iron and copper in cured tobacco are 435-605 and 18-40 μg/g, respectively [2], which is below the concentration added to cigarettes before smoking.

It is also evident that decrease of phenols content is more pronounced for the cigarettes of the IV quality group whose phenols content is much higher before the metal salt addition. In order to make better comparison of the individual metal salts effect, in Fig.1. and Fig.2. we present the same data together with the relative values (the values for cigarettes with no addition are taken to be 100%) for the mass of tar, and CO content of mainstream cigarette smoke for the cigarettes of the I and IV quality group, respectively.

Considering the results shown on Fig.1. and Fig.2 we may conclude that the greatest efficacy in reducing the measured quantities was generally achieved by the addition of $CuCl_2$. However, in some cases (for the I quality group cigarettes) the addition of $FeCl_3$ is equally, or even slightly more effective. Similar results for the addition of $CuCl_2$ and $FeCl_3$ may be explained by the fact that both Cu(II) and Fe(III) ions are oxidizing agents. The effect of $FeCl_2$ is less pronounced than that of $CuCl_2$ or $FeCl_3$, but still significant in comparison with the relative error of measurements (indicated by the vertical bars on the values for cigarettes without addition in both Fig.1 and Fig.2). The decrease of phenols content in CSC by the addition of $CuCl_2$ or $FeCl_3$, and to lesser extent $FeCl_2$, may be the consequence of some catalytic reactions during smoking. We can not rule out either the possibility that volatile phenols are at least partly bonded to metal ions during pyrolytic

reactions by forming ionic associates or complexes.

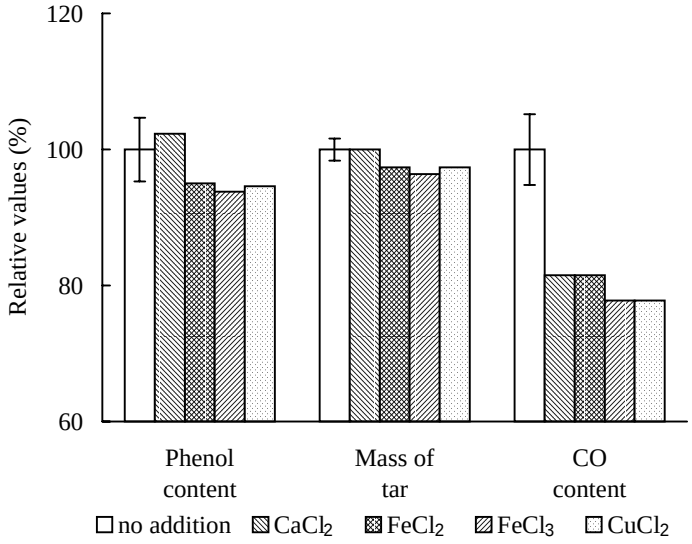

Fig.1. The change of phenols content, mass of tar, and CO content by the addition of metal salts (1mg of metal ion/cigarette) to the cigarettes of the I quality group.

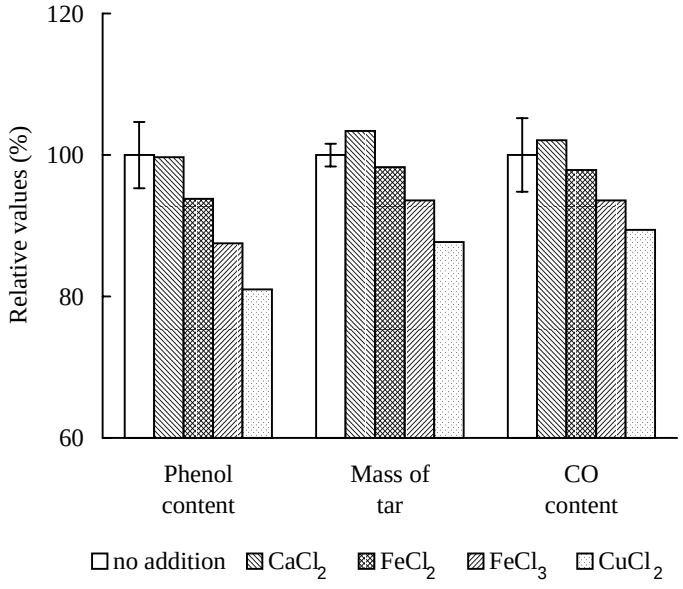

Fig.2. The change of phenols content, mass of tar, and CO content by the addition of metal salts (1mg of metal ion/cigarette) to the cigarettes of the IV quality group.

Chloride ion effect on the phenols content of CSC could not be considered significant in view of the results obtained by the $CaCl_2$ addition to cigarettes before smoking. However, large decrease of CO content (about 20%) in the mainstream smoke of the I quality group cigarettes with the addition of all metal chlorides used in this study may be indicative of its influence on general smoking conditions [1,2].

4. CONCLUSIONS

The results of this study show that addition of some inorganic metal salts to cigarettes before smoking may reduce the phenols content of CSC by up to 20%. The mass of tar and CO content are also reduced, and these results clearly warrant further research. Beside the possible practical implications, additional work may contribute to better understanding of pyrolytic conversion of various tobacco constituents to phenolic compounds during smoking.

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UTICAJ DODATKA METALNIH SOLI CIGARETAMA PRE PUŠENJA NA SADRŽAJ ISPARLJIVIH FENOLA U KONDENZATU DUVANSKOG DIMA

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Fenolna jedinjenja su vrlo značajni sastojci kondenzata duvanskog dima (KDD) jer utiču na aromu, ukus i fiziološka svojstva duvanskog dima. Mnoga od tih jedinjenja su toksična. U ovom

radu je ispitivan uticaj dodatka $CaCl_2$, $FeCl_2$, $FeCl_3$ i $CuCl_2$ cigaretama pre pušenja na sadržaj isparljivih fenola u KDD. U nekim slučajevima sadržaj fenola u KDD je značajno smanjen (i do 20%) kao i masa katrana i sadržaj CO u glavnoj struji duvanskog dima.

Ključne reči: *kodenzat duvanskog dima, fenoli, soli metala*