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GAS CHROMATOGRAPHIC ANALYSIS OF SOME TOXIC ORGANIC COMPOUNDS IN MAINSTREAM CIGARETTE SMOKE

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Abstract. *In order to protect the human health from harmful effects of smoking, we consider the magnitude and range in levels of various groups of toxic organic compounds: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phenols and chloroorganic pesticides in mainstream cigarette smoke, obtained from Yugoslav blend cigarette. The cigarette smoke condensate was collected with electrostatic condensation on Cambridge filter pad and extracted it with organic solvent, and then subjected to gas chromatographic (GC) analysis.*

Keywords: *Cigarette smoke; PAHs, PCBs, phenols, pesticides; GC analysis.*

INTRODUCTION

Inside a burning cigarette, a large variety of physical and chemical processes are occurring in an oxygen-deficient, hydrogen-rich environment with temperatures as high as 950 ^{o}C. As result of these processes is a very complex aerosol, which consists of organic and inorganic molecules, dispersed in a matrix of the atmospheric gases. Many of them are toxic, contributing mainly to strong carcinogenic effect of cigarette smoke [1].

On the various classes of organic compounds found in cigarette smoke condensate (CSC), the polycyclic aromatic hydrocarbons (PAH_S) are of particular interest because of the cancerogenic activity of some members of this family. The carcinogenic activity of a particular compound is very dependent on its structure.The addition of substituent groups in favorable position in certain PAHs often have an activating influence [2-5].

The concentration values of some phenol compounds, also are very important,

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because they have considerable role in tumor forming. Relative value of phenol cancerogenity in CSC is as follows [6,7]: phenol, 2-, 3-, 4-methylphenol, 2,4-, 2,5-, 3,4- i 3,5-dimethylphenol are very active; 2-ethylphenol is medium activity, and 2-hydroxyphenol, 4-methoxyphenol hydrochinone are inactive.

Wide spectrum of toxic polychlorinated biphenyls (PCB_S) and chloroorganic pesticides are released into CSC as a result of either industrial and agricultural activities. A determination of PCBs and residue pesticides is of special interest for tobacco industry [8,9].

The possibly toxic organic compounds in CSC are extensively studied and many analytical methods are developed for their separation and quantification. These compounds are determined by combination of gas, liquid, paper and thin-layer chromatographies and infrared, ultraviolet, fluorescence and mass spectrometries. The development of capillary column gas chromatography suitable for the separation of organic compounds provides the necessary degree of resolution to separate and identify trace of toxic organic constituents in CSC [10-16].

In order to protect the human health from harmful effects of smoking, in this paper we report quantitative methods for the separation and identification of major PAHs, PCBs, phenols and pesticides in CSC, obtained from Yugoslav blend cigarette.

EXPERIMENTAL

A. Materials

All solvents were spectrograde and obtained from Merck (Germany). The other chemicals were reagent grade.

The PAHs, PCBs, phenols and pesticides standards used for determination of GC response data were purified by chromatography on a short silica gel column.

Investigated cigarettes were obtained from the Tobacco Research Institute-Niš (Yugoslavia) and conditioned at 60% relative humidity for at least 48 hours.

The results were mean of five measurements. The average relative standard deviation was 5,1%.

B. Apparatus

The chemical composition of the examined blend cigarette was established by standard *Coresta* methods [17]. Prepared blend cigarette was smoked with a 30-channel automatic RM 20 Borgwaldt smoker (Germany) for collection of the mainstream smoke.
A Perkin Elmer 8500 gas chromatograph (USA) with flame ionization detector (FID) was used for quantitative analysis of PAHs and phenols, and electron capture detector (ECD) was used for quantitative determined of PCBs and pesticides.

C. Cigarette Smoke Collection

The investigated cigarette after being conditioned was smoked to a 30 mm butt length on a 30-port Borgwald smoking machine under the standard smoking conditions: 2-second puff duration, 1 puff/min and 35-ml draw/puff [18].

The condensate of 20 cigarettes from each group was collected on *Cambridge* filter

pad by procedures described by Pillsbury et al [19] and Johnson et al [20], respectively.

D. Isolation procedure

The CSC collected on *Cambridge* pad was Soxhlet-extracted for 10 h with 250 ml *n*-hexane. The neutral CSC fraction was obtained by the acid - base extraction internal procedure (Figure 1).

The PAH-containing fraction was cleaned up by column chromatography on neutral silica gel (60- 150 mesh) previously dried for 4 h at 160 ^{o}C and stored in a desiccator over self-indicating 8 -mesh anhydrous calcium sulfate. *n*-Hexane was used as the eluent at a flow rate of 2 ml/min.

The phenols were extracted with methanol, and PBCs and residue of pesticides with methylenechloride.

E. Gas Chromatographic Analysis

Gas chromatographic (GC) analysis was performed under the gas chromatographic conditions:

Column: 30 m × 0.25 mm i.d. glass cappillary SPB-5 packed with Chromosorb WHP (100/120 mesh);

Carrier gas: Nitrogen at a flow rate of 1 ml/min;

Column temperature: 90 - 300 ^{o}C (at 2 ^{o}/min);

Detector: Flame ionization detector (FID) and electrone capture detector (ECD);

Injector and detector temperature: 290 ^{o}C and 350 ^{o}C, respectively;

Split ratio: 1/50.

RESULTS AND DISCUSSION

One of the most important requirements in the tobacco industry is the ability to control for toxic organic compounds in the cigarette smoke.

Considerable quantities of toxic organic compounds are formed in the pyrolysis, pyrosynthesis and distillation zone just downstream of the combustion zone. In Table 1 are listed 15 classes of organic compounds and number of different components which have been reported in zones [7]. There is a total of 4720 compounds. The miniature chemical factory known as a cigarette converts tobacco into what may be the most complicated, most complex collection of organic compounds to be found.

In this work, the investigated cigarette can be considered as a typical representative of the Yugoslav blends (blend cigarette) made only of domestic tobacco varieties. The main chemical composition of this cigarette is given in Table 2.

Typical procedures for separating and determining organic traces in CSC involve the use of at least one solvent-partitioning step. Solvents such as cyclohexane or hexane are used to isolate the PAHs and aliphatic hydrocarbons (ALHs) as one fraction from aqueous methanol.

The use of a four - step isolation procedure (Figure 1) assures quantitative PAHs recovery from small quantities of CSC. This method involves the use of acid - base extraction in order to separate acid - soluble and base - soluble components from the

CSC, after which a neutral fraction containing the PAHs and ALHs is obtained by partitioning into hexane.

Table 1. Approximate number of organic compounds identified in some major organic compound classes

Classes	Number
Amides, imides, lactams	237
Carboxylic acids	227
Lactones	150
Esters	474
Aldehydes	108
Ketones	521
Alcohols	379
Phenols	282
Amines	196
N-Heterocycles	921
Hydrocarbons	755
Nitriles	106
Anhydrides	11
Carbohydrates	42
Ethers	311
Total	4720

Table 2. Main chemical composition of the investigated Yugoslav blend cigarette

Chemical composition	Blend cigarette
Cigarette mass (g)	0,996
Cigarette humidity (%)	11,22
Nicotine (%)	1,36
Total nitrogen (%)	2,86
Proteins (%)	8,21
Soluble sugars (%)	7,97
Potassium (mg/g)	19,78
Calcium (mg/g)	37,29
Magnesium (mg/g)	7,33
pH	6,43

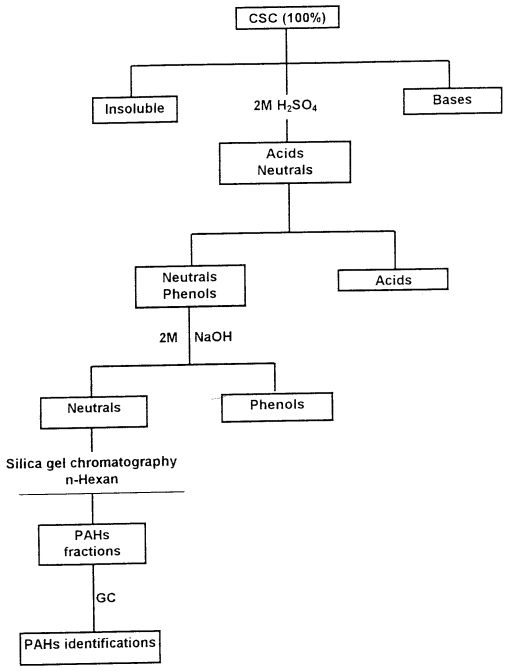

Fig 1. Isolation scheme for small quantities of cigarette smoke condensate

The quantities of selected PAHs in CSC from Yugoslav blend cigarette are listed in Table 3 [21]. Values are given for PAHs in ng/cigarette over the total PAHs range from naphthalene to benzo[*ghi*]perylene. The value of 8.6 ng/cigarette for benzo[*a*]pyrene for Yugoslav cigarette is in good agreement with 9.2 ng/cigarette for Kentucky reference 1R4F cigarette found by C. Risner [22] and 13.4 ng/cigarette for a UK cigarettes found by W. H. Evans et al [23].

Table 3. Average values of selected polycyclic aromatic hydrocarbons (PAHs) in cigarette smoke of investigated Yugoslav blend cigarette (μg/g)

PAHs (μg/g)	Blend cigarette
Naphthalene	1,1351
Acenaphthylene	0,2936
Acenaphthene	0,1218
Fluorene	0,1056
Phenanthrene	0,0210
Anthracene	0,0440
Fluoranthene	0,0270
Pyrene	0,0377
Benzo[a]anthracene	0,0095
Benzo[a]pyrene	0,0086
Benzo[ghi]perylene	0,0005
Total	1,8043

The values for some phenol derivatives in CSC are given in Table 4. It is obvious, that the best way of cigarette smoke collection for these compounds is *via Cambridge* filter and after that extraction with methanol [24].

Table 4. Average values of some phenol derivatives in cigarette smoke of investigated Yugoslav blend cigarette (mg/g)

Chloroorganic pesticides (μg/g)	Blend cigarette
HCH	0,1291
Lindane	0,0390
Heptachloro	0,0000
Aldrine	0,2107
Heptachloroepoxide	0,0000
Endosulphane-α	0,0000
Endosulphane-β	0,0875
Dieldrine	0,0000
DDT	0,0318
Total	0,4981

Polychlorinated biphenyls comprise a series of biphenyl homologues differing in the degree of chlorine substitution (Table 5). The concentration of these compounds and of the residue pesticides (Table 6) in CSC seem to be within the range found in the literature [7, 9, 16].

The best method of cigarette smoke collection for these compounds, also is *via Cambridge* filter and after that extraction with methylenechloride.

Table 5. Average values some chloroorganic pesticides in cigarette smoke of investigated Yugoslav blend cigarette (μg/g)

PCBs (μg/g)	Blend cigarette
2-Chlorobiphenyl	0,0000
3,3-Dichlorobiphenyl	0,0781
2,2,5-Trichlorobiphenyl	0,0000
2,2',4,4'-Tetrachlorobiphenyl	0,0495
2,3',4,5',6 –Pentachlorobiphenyl	0,0270
2,2',3,3',6,6'-Heksachlorobiphenyl	0,0146
2,2',3,4,5,5',6 –Heptachlorobiphenyl	0,0000
2,2',3,3',4,4',5,5'-Octachlorobiphenyl	0,0130
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	0,0023
2,2',3,3',4,4',5,5',6,6'-Decachlorobiphenyl	0,0032
Total	0,1877

Table 6. Average values of some polychlorinated biphenyls (PCBs) in cigarette smoke of investigated Yugoslav blend cigarette (μg/g)

Phenols (mg/g)	Blend cigarette
Phenol	0,0742
2-Chlorophenol	0,0701
2-Methylphenol	0,0000
2-Nitrophenol	0,0146
4-Nitrophenol	0,0395
2,4-Dichlorophenol	0,0451
2,4-Dimethylphenol	0,0049
2,4-Dinitrophenol	0,0000
4-Chloro-3-methylphenol	0,0532
2-Methyl-4,6-dinitrophenol	0,0000
2,4,6- Trichlorophenol	1,0926
Pentachlorophenol	0,0147
Benzophenol	0,0173
Total	1,4174

The confirmation of the investigated compounds identities was accomplished by comparison of the GC relative retention times with those of standards compounds.

CONCLUSIONS

Quantities of some PAHs, PBCs, phenols and pesticides in CSC from Yugoslav blend cigarette are obtained, by appliance of combined method for collecting of CSC (*Cambridge* filter and solvent trap) and GC analysis.

The results show that investigated compounds are in the limits presented in the literature for various tobacco blends.

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GASNO HROMATOGRAFSKA ANALIZA NEKIH TOKSIČNIH ORGANSKIH JEDINJENJA U GLAVNOJ STRUJI CIGARETNOG DIMA

B. Stojčeva Radovanović, Z. Mišić

U cilju zaštite čovekovog zdravlja od štetnih efekata pušenja, ispitivane su koncentracije različitih toksičnih organskih jedinjenja: policikličnih organskih jedinjenja (PAH), polihlorovanih bifenila (PCB), fenola i organohlornih pesticida, u glavnoj struji cigaretnog dima dobijenog od jugoslovenske blend cigarete. Kondenzat cigaretnog dima je sakupljen elektrostatičkom kondenzacijom na Cambridge filteru i ekstrahovan organskim rastvaračima, a zatim podvrgnut gasnohromatografskoj (GC) analizi.

Ključne reči: *cigaretni dim; PAH, PCB, fenoli, pesticidi, GC analiza*