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Investigation of organometallic compounds adsorption in cigarette smoke via extracted humic acid

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Abstract: Cigarette smoke contains organometallic compounds of Cr, Pb, Ni, Co, As, Se and V**.** Consumption of cigarette causes to exchange of Ca, Zn and Fe in body by these metals or association of them and derange of body systems.Humic acid (HA) contains functional groups such as COOH, (OH), C=O and connect easily with multivalence cation, chelate groups and some oxides. Humic acid is appropriate absorbent for metal compounds. In this study humic acid was extracted from soil then leachated and added to cigarette filter. Organometallic compounds are adsorbed on the humic acid extracted by methanol and then studied by Gas Chromatography/Mass Spectrometry (GC-MS). The results of this study identifed organochelate compounds of carbonyl, alkyl, acetate, halide, cyclic, alken, phenyl and alkaloid. At last about 60 organometal compounds adsorbed by HA. Adsorption order of organometallic compounds so as follow:

Boron>Iron>Cobalt>Manganese>Aluminum>Chromium>Lead>Selenium>Tin>Copper>Vanadium>Cesium>Germanium, Zinc, Nickel, Bismuth, Titanium, Arsenic, Molybdenum, Thallium, Rhodium, Tellurium, Rhenium

Keywords: Humic Acid, Organometallic Compounds, Cigarette Smoke, Adsorption , GC/MS.

Introduction

Tobacco contains metallic compounds that absorbed from weather and soil [1] and then change to organometallic compounds. Cigarette smoke contains organometallic compounds of Cr, Pb, Ni, Co, As, Se, V [2,3]. These compounds change or derange of body organs such as brain, nerve, blood vessels, heart vessels, exocrine glands, enzymes, digestive and security systems, reproduction and urinary channels [4] and exchange of Ca, Zn, and Fe in body by these metals or association of them and or derange of body systems [5]. Theses must be reduced compounds.

Humic acid (HA) contains some functional groups such as COOH, phenolic (OH), alcohol (OH), C=O and associate easily with multivalence cation and chelate groups [6]. Humic acid is appropriate adsorbent for metallic compounds (MC) [7-9].

The structure suggested by Stevenson (in 1982) [10] shows that phenol groups with free OH, kinolynic structure, heterocyclic compounds and some COOH groups bond to aromatic nucleus (Stevenson Structure model) (Figure **2**).

HA have active functional groups that can adsorbent organic compounds such as color and phosphorous organic poisons and colors contaminant compounds [11-15].

HA has a suitable ability for adsorption of metal and organic compounds, consequently it can be one of the important adsorptive for contaminant [16].

Result and Discussion

Study of AH SEM before and after of cigarette smoking, showed that the adsorption of compound on HA. Chromatogram (Digram **1**) and Table **1** show to HA adsorbent easily a lot of organometallic compounds with different molecular structure. HA adsorbent of 60 metal compounds (MC) compounds from cigarette smokes. According to the data in Table **1** conclude that HA can adsorbe some important organometallic compounds such as V, As, Ti, Pb, Cs, Re, Tl, Ro, Co, Se, Mo, Ni,

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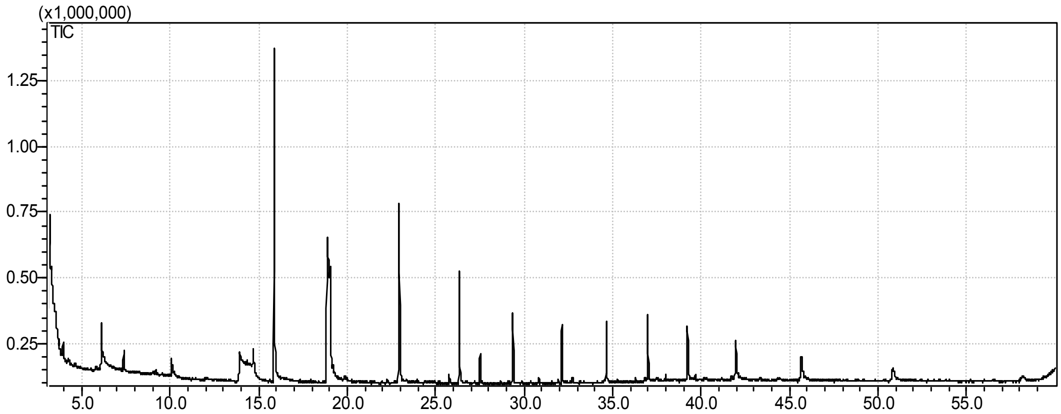
Cr, Ta, Ga. These adsorbed molecules have high molecular weight and large molecular structure (Figure **1**). Study of Chromatogram was showed high absorption for organo compounds of B,Fe, Mn, Al, Cr, Pb, Se and Sn in cigarette smoke.



Digram 1. Chromatogram of adsorption compound by HA

Conclusion

The results show that MC in cigarette smoke. Most of chelate are compounds of carbonyl, alkyl, acetate, halide, cyclic, alken, phenyl, alkaloid, carbonyl and aldehyde. Heavy metals in cigarette smoke have chelate of acetate, phenyl, alcohol and alken groups (Sn, Cu, Pb). Metal complexes such as Rh, Re, Mo in cigarette smoke show there are in soil and go inside to tobacco plants.

Result of this study show HA can to adsorb a lot of MC that Limit 60 organometallic compounds adsorbent by a little of HA. As showed in Table **1** adsorption arrangements so as follow:

Boron > Iron> Cobalt > Manganese >Aluminum > Chromium > Lead > Selenium > Tin> Copper > Vanadium > Cesium > Germanium, Zinc, Nickel, Bismuth, Molybdenum, Titanium, Arsenic, Thallium, Rhodium, Tellurium, Rhenium.

Table 1. Compounds of adsorbent on HA

Component Name	Molecular formula	Molecular Weight
Borancarbonyl	CH_3BO	42
Boranethyl dimetyl _Me$_2$B_ET	$C_4H_{11}B$	70
Bronoic acid ethyl	$C_2H_7BO_2$	74
Aluminuim triethyl	$C_6H_{15}AL$	114
2,5-Dimethylethylcyclo-tetrazonoboran	$C_4H_{11}BN_4$	126
2-Ethyl-5-methyl-1,3,5-oxathicoborolane	$C_5H_{11}BOS$	130
Germyl mono thio acetat	C_2H_6GeOS	152
Zinc allyl crotyl	$C_7H_{12}Zn$	160
Nickel tetra carbonyl	C_6CrO_6	170
Caesium acetat	$C_2H_3CsO_2$	192
Aluminium triisobutryl	$C_{12}H_{27}AL$	198
Cobalt tetra carbonyl Silyl	$C_4H_3Co_4Si$	202
Mangenes tricarbonyl[(1,2,3,4,5,eta)(i-H-pyrol-1-yl)]	$C_7H_4MnNO_3$	205
Vanadium(7cycloheptatrienylium(2,4,5-cyclopentadien)	$C_{12}H_{12}V$	207
1-pyrol-1.1'.1"-borylidynetris	$C_{12}H_{12}BN_3$	209

Boron-hexahydro-2H-azepin-2-onato-N-O,2-methyl ethyl	$C_{12}H_{24}BNO$	209
Mangenese penta carbonyl methyl	$C_6H_3MnO_5$	210
Chromium carbonyl	C_6CrO_6	220
Iron tricarbonyl (0,1,2,3-eta)-methyl-2-propenoate	$C_7H_6FeO_5$	226
Tri-tert-butylborat	$C_{12}H_{27}BO_3$	230
Vanadium-pentacarbonyl(eta-2,3,-propenyl)	$C_8H_5O_5V$	232
Propanoic acid-2,2-dimethyl cesium	$C_5H_9CsO_2$	234
Caprolactoneoxime(NB)-O[diethyl boryloxyl(ethyl)borty]	$C_{12}H_{25}B_2NO$	237
Mangenese_acethyl penta carbonyl	$C_7H_3MnO_6$	238
Bis(eta-4-cyclohexadiene) manganese carbonyl	$C_{13}H_{16}MnO$	243
Iron tetra carbonyl (pyridine)-(tb-5-12)	$C_9H_5FeNO_4$	247
Mangenese tricarbonyl(1,2,3,4,5_eta)-1-(dimethylamino)methyl-2,4-cyclo pentadien-1-yl	$C_{11}H_{12}MnNO_3$	261
Asetonitrile-2-chloro-2-(dimethylamine(N_B)-bis(trifluoromethyl)boryl	$C_6H_8BClF_6N_2$	268
Irontetracarbonyl-2-(dimetylamino)ethylphosphin	$C_8H_{12}FeNO_4P$	273
Dimetyl aluminium piperidin	$C_{14}H_{32}AL_2N_2$	282
4-Phenyl seleno-6-oxabi cyclo-octan-7-one	$C_{13}H_{14}O_2Se$	282
Phenanthro(1,2,3)-(1,2,5)selenadiazol	$C_{14}H_8N_2Se$	284
Methylbenzoate (dicarbonyl)thiocarbonyl chromium	$C_{11}H_8CrO_4S$	288
Lead diethyl dimethyl	$C_6H_{16}Pb$	296
Bismuthinue triethyl	$C_6H_{15}Bi$	296
Stannanetrimethyl[(triflouromethyl-sulfinyl)oxy]	$C_4H_5F_3O_2SSN$	298
Irontricarbonyl[N,N'-1,2-ethandiylidenebis[2-methyl-2-propanamin]-N,N']	$C_{13}H_{20}FeN_2O_3$	308
Iron tetracarbonyl [(2,3,eta)-dimetyl-2-butenedioate	$C_{10}H_8FeO_8$	312
1-5-Cyclo octandiy(boryl)laurinl octan	$C_2OH_{36}BNO$	317
Molibdenum-pentacarbonyl (pyridazine)-(OC-6,2,2)	$C_9H_4MoN_2O_5$	318
Lead acetic acid	$C_4H_6O_4Pb$	326
Titanium(IV) butoxide	$C_{16}H_{36}OTi$	340
Cobalt_eta,5_cyclo penta dienyl eta5-1,2-di phenyl cyclo pentanyle	$C_{22}H_{18}Co$	341
Copper(II)-2,9-diacetyl-1,10-dimetyl -4,7diazadeca-2,9diene-1,10-dione	$C_{14}H_{18}CuN_2O_4$	341
Dicobalt octa carbonyl	$C_8Co_2O_8$	342
Arsenousacid tris(trimethysily) ester	$C_9H_{27}AsO_3Si_3$	342
Chromium renta carbonyl(1,3,5,7-cyclo octa tetraneldi	$C_{13}H_8Cr_2O_5$	348
Thallium(Triacetyl)Methyl	$C_7H_9O_3Tl$	349
Phenyl cyclopenta dienyl--bis-trimethyl phosphine cobalt	$C_{17}H_{27}CoP_2$	352
6-Cyano-4,7-diPhenyl-1,2,5-selenadiazol-3,4-pyridine	$C_{18}H_{10}N_4Se$	362
Rhodium carbonyl chloride	$C_4Cl_2O_4Rh_2$	388

2,2-Diphenyl-1,2,3-benzo-dioxa-4H-tellurine	$C_{19}H_{16}O_2Te$	406
Lead tetra acetate	$C_8H_{12}O_8Pb$	444
Stanane-1,3-dithian-2-ylidene bis(trimethyl)	$C_{10}H_{24}S_2Sn_2$	448
Bis(trimethylstanny)adamantan	$C_{16}H_{32}SN_2$	464
Bis(1,2,bis)diisoprorylphosohino ethane-dihydro cobalt	$C_{26}H_{68}Co_2P_4$	464
Iron decarbonyl tri(ethyne)	$C_{12}H_2Fe_3O_{10}$	474
Copperbis(1,3-diphenyl-1,3-propanedionato-o,o')(SP-4,1)	$C_3OH_{22}CuO_4$	509
(Mu-Bromo)[mu-eta-1:.eta_2_(2-fluoranthyl) vinyl]bis(tricarbonyliron)(fe-fe)	$C_{24}H_{11}BrFe_2O_6$	586
Di rhenium-decarbonyl	$C_{10}O_{10}Re_2$	654

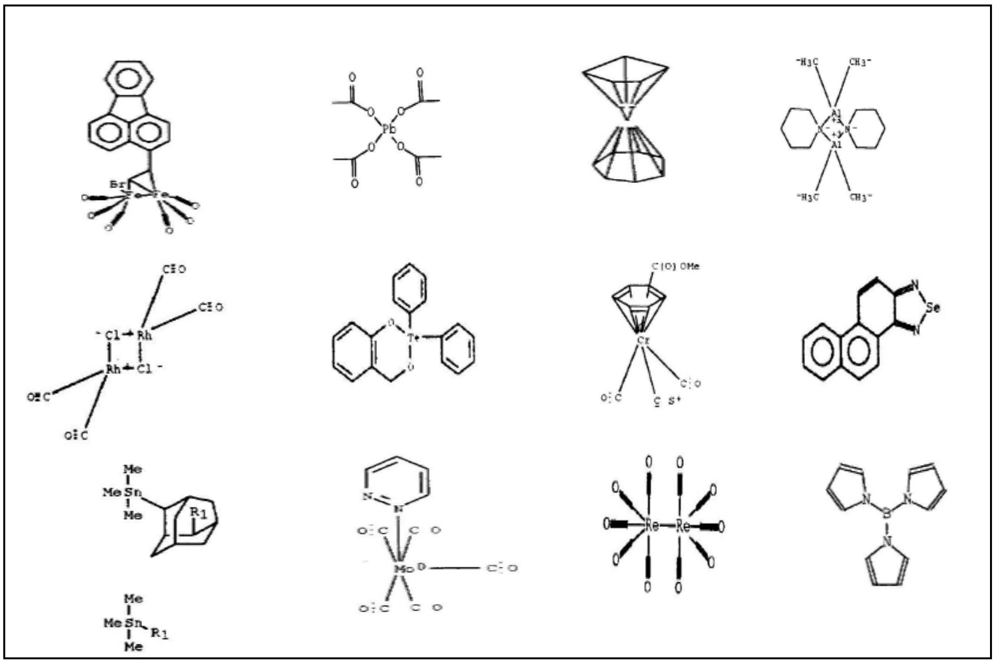


Figure 1. Molecular structure of some organometallic compounds of cigarette smoke adsorption on humic acid

Experimental

Chemicals

High purity double deionizer water (18mΩ^{-1}cm^{-1}) was obtained from a milli-Q50 SP water purification system (Millipore Corporation, USA). HPLC grade methanol, Ethanol (96%), NaOH and HCl were supplied from Merck Company. Pite soil was from Noshahr forest with black brown color.

Apparatus

Gas Chromatography-Mass Spectrometry (GC/MS) was Shimadzo 2010 GC system coupled whit a Shimadzo 2010 quadruple Mass Spectrometer wiht Helium (99.999%) as a carrier gas. Analysis using a J&W DB-5 ms capillary column of 30m * 0.25mm I.D. Smoke machine system is Filtrona CSM and shaker system is Gerhardt ISZ.

Procedure

HA was extracted from Noshahr forest soil after analyses (Table **2**). Forest soil was dried and screened by 2mm sieve and then analyzed. 50Gr from soil was weighted, and added to 200ml NaOH (0.1 M/L) and then was shaked for 3 hours at room temperature and filtrated. HCl (0.1 M/L) was added at solution until adjusted pH between 2-2.5.After 2 hours , HA deposit was filtered and washed by 50ml ethanol for thrice and dried into oven (50^{o}C for 24 hours). Particle size of HA determined by microscope that show about 30 micron (Figure **3**).

HA was weighted 5g into 250ml flask, added 100ml pure methanol and shake for 6 hours and then filtrated and dried. 30mgr HA was weighted and added to cigarette filter. 20 cigarettes were smoked under standard condition by smoking machine. The Scanning electron microscope (SEM) of HA are shows in Figures **4** and **5**.

The fresh tar was extracted by shaking of HA in pure methanol for 8 hours and immediately measure by GC/MS. The temperature program was used as following condition:

Temperature program : (60^{o}C , for 0.5 min, 250^{o}C at 5^{o}C /min, 250^{o}C for 20 min, 300^{o}C at 30^{o}C /min, 300^{o}C for 7min)

Oven temperature: 60^{o}C, flow: 0.8 ml/min, Ion source temperature: 200^{o}C, interface temperature: 270 ^{o}C.

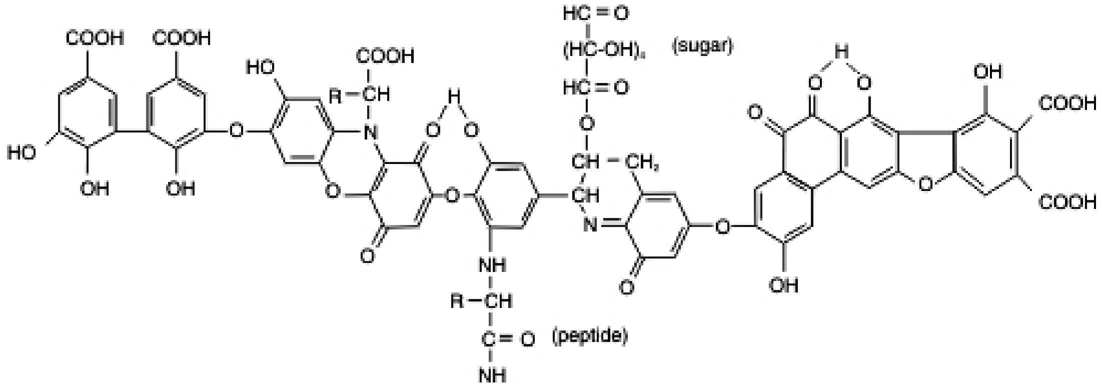


Figure 2- Model structure of HA (Stevenson 1982)

Table 2. Chemichal analysis of Noshahr soil

OC (%)	N (%)	PH	C/N	Na(ppm)	K(ppm)	P(ppm)	Electrical Conductivity
13.7	2.06	7.20	6.65	294.7	532.6	15	1.07

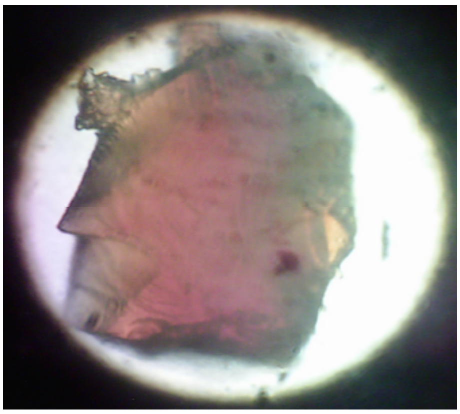


Figure 3. Microscope scheme of HA crystal particles with 30 micron diameter (40 time magnification)

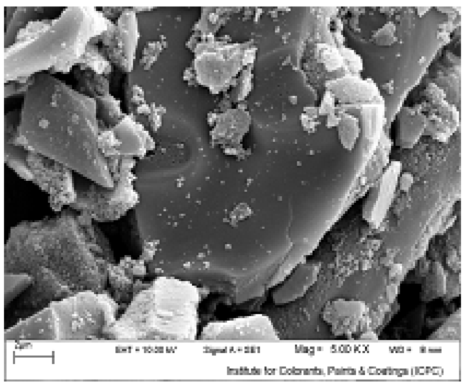


Figure 4. HA SEM before adsorption of compounds

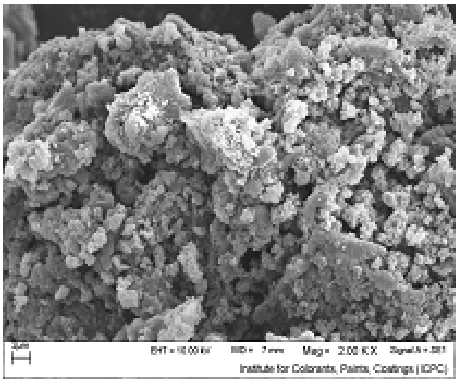


Figure 5. HA SEM after adsorption of compounds

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