

## The effect of synthesized alumino silicagel for adsorption of organic compounds from cigarette smoke

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**Abstract:** Organic compounds are the most important chemical composition in cigarette smoke. 10Mg of alumino silicagel synthesized from alumina and sodium silicate putted in cigarette filter and smoked by smoking machine. Absorbent compound extracted by pure methanol and characterized via GC/MS. Result showed adsorption of aromatic, nitrous, sulfide, cyanides and amine compounds. Highest adsorption of organic compounds was related to polyaromatic hydrocarbons (PAHS), cyanides and hydrazine's derivatives. Alumino silicagel has ability for adsorption of organic compounds because of its poly silica and aluminosilica structure.

**Keywords:** Micro silica, Gas chromatography mass spectroscopy, GC/MS method, Aluminosilicagel, Organic compounds.

### Introduction

Tobacco has been used by humans for thousands of years in a variety of forms. Environmental tobacco smoke (ETS) was classified as Group A carcinogen by USEPA [1]. Malignant neoplasms (e.g., lung cancer) and other chronic diseases (e.g., heart disease and chronic obstructive pulmonary disease) have been shown to be associated with smoking by epidemiological studies [2] and also were regarded as an important source for increasing indoor pollutants [3,4]. ETS is a complex aerosol comprising over 5200 identified chemicals present in both particulate and vapor phases [5]. It is formed when tobacco, itself a complex mixture of over 2000 chemical constituents [6], is burnt incompletely during the smoking of the cigarettes. Inside the burning cigarette the tobacco is exposed to temperatures ranging from ambient temperature up to approximately 950 °C, in the presence of varying concentrations of oxygen. Thousands of chemical substances are generated, many of which arise from several distinct mechanistic routes,

as demonstrated by studies carried out by Baker [7]. The gas phase of a non-filter cigarette consists of nearly 500 individual volatile compounds, including carbon monoxide, nitrogen oxides, cyanide and ammonia and comprises roughly 95% of the weight of mainstream cigarette smoke (MCS) [8]. The particulate phase contains more than 3500 semivolatile and nonvolatile individual compounds, including nicotine, polynuclear aromatic hydrocarbons (PAHs) [8] and halogenated aromatic hydrocarbons (HAHs) [9-12]. Composition of both gas and particulate phases vary with a broad range of cigarette design features [13]. Important compounds in MCS are PAHs which contain the ring of benzene cyclic. Therefore, techniques to remove undesirable components for tobacco taste and health have been developed without losing an essential taste of cigarette. One of the promising methods for this purpose is incorporation of appropriate adsorbents in cigarette filters. Silicified regions in the stem and leaf of the horsetail *Equisetum arvense* were studied by scanning and transmission electron microscopy. The silica was present as a thin

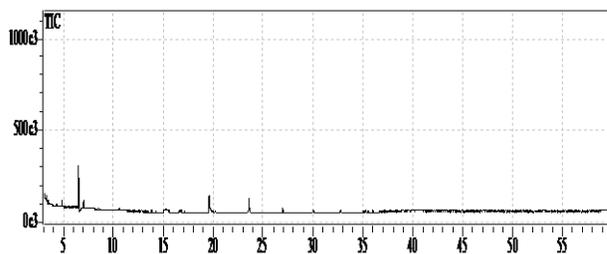
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layer on the outer surface with variation in the size of this layer depending on the part investigated. There was a dense arrangement of silica spheres with some density fluctuations. A loose arrangement of silica particles with variation in their size was found beneath this dense arrangement suggesting the agglomeration of silica. An electron diffraction pattern showed the presence of amorphous silica, with the short range order being comparable to that of silica from other chemical sources [14]. Silica gel is a granular, vitreous, porous form of silica made synthetically from sodium silicate. Despite its name, silica gel is a solid. It is a naturally occurring mineral that is purified and processed into either granular or beaded form. As a desiccant, it has an average pore size of 2.4 nanometers and has a strong affinity for water. Silica gel is most commonly encountered in everyday life as beads packed in a vapor-permeable plastic. In this form, it is used as a desiccant to control local humidity in order to avoid spoilage or degradation of some goods. Because of poisonous dopants and their very high absorption of moisture, silica gel packets usually bear warnings for the user not to eat the contents. Silica gel was in existence as early as the 1640s as a scientific curiosity [15]. It was used in World War I for the absorption of vapors and gases in gas mask canisters. The synthetic route for producing silica gel was patented by chemistry professor Walter A. Patrick at Johns Hopkins University, Baltimore, Maryland, USA in 1919. In World War II, silica gel was indispensable in the war effort for keeping penicillin dry, protecting military equipment from moisture damage, as a fluid cracking catalyst for the production of high octane gasoline, and as a catalyst support for the manufacture of butadiene from ethanol, feedstock for the synthetic rubber program. Silica gel's high surface area (around 800 m<sup>2</sup>/g) allows it to absorb water readily, making it useful as a desiccant (drying agent). Once saturated with water, the gel can be regenerated by heating it to 120 °C (250 °F) for two hours. Some types of silica gel will "pop" when exposed to enough water. This is caused by breakage of the silica spheres when contacting the water [16]. A solution of sodium silicate is acidified to produce a gelatinous precipitate that is washed and then dehydrated to produce colorless silica gel. When a visible indication of the moisture content of the silica gel is required, ammonium tetrachlorocobaltate (II) (NH<sub>4</sub>)<sub>2</sub>CoCl<sub>4</sub> or cobalt chloride CoCl<sub>2</sub> is added [16]. This will cause the gel to be blue when dry and pink when hydrated [16]. An alternative indicator is methyl violet which is orange when dry and green when hydrated. Silica gel is non-toxic, non-

flammable, and non-reactive and stable with ordinary usage. It will react with hydrogen fluoride, fluorine, oxygen difluoride, chlorine trifluoride, strong acids, strong bases, and oxidizers. Silica gel is irritating to the respiratory tract and may cause irritation of the digestive tract, and dust from the beads may cause irritation to the skin and eyes, so precautions should be taken. Some of the beads may be doped with a moisture indicator, such as cobalt(II) chloride, which is toxic and may be carcinogenic. Cobalt (II) chloride is deep blue when dry (anhydrous) and pink when moist (hydrated). Crystalline silica dust can cause silicosis but synthetic amorphous silica gel is non-friable, and so does not cause silicosis. Silicagel has ability to adsorb some chemical compound in cigarette smoke. In this study adsorption of organic compounds in cigarette mainstream smoke has been investigated.

## Results and discussion

The GC spectrum of cigarette compound adsorbed on aluminosilicagel (Figure 1) was studied.



**Figure 1:** GC spectrum of cigarette compound absorption on aluminosilicagel.

Study of GC spectrum by WILLY229 and NIST libraries showed that most important compounds adsorbed on aluminosilicagel (Table 1).

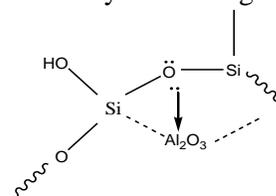
**Table 1.** Absorbed organic compounds on aluminosilicagel

Entry	Compound names	Formula	Mol. weight	Structure
1	2-Benzyl-4-methyl phenol	C <sub>14</sub> H <sub>14</sub> O	198	
2	9-(4-Tolylamino) phenanthren	C <sub>21</sub> H <sub>17</sub> N	283	
3	10-Heptyl-10-hydroxy-9(10H)-anthracenone	C <sub>21</sub> H <sub>24</sub> O <sub>2</sub>	308	
4	2,3-Diphenyl quinoxaline	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub>	282	
5	N-Nitroso dimethyl	C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O	74	

	amine(DMN)					
6	Diallyl sulfone	$C_6H_{10}O_2S$	146		27	Hydrazine carboxamid
7	(2E)-2-(Hydroxyimino)ethyl acetate	$C_7H_7NO_3$	117		$CH_3N_3O$	75
8	1-Chloro-2-methylaziridine	$C_3H_6ClN$	91			
9	5H-Benzo[def]carbazole	$C_{14}H_9N$	191			
10	9-N-Dodecylanthracene	$C_{26}H_{34}$	346			
11	1-Benzene sulfonyl-1-H-pyrol	$C_{10}H_9NO_2S$	207			
12	1,2-Epoxy-3,4-dihydroxycyclohexano[a]perene	$C_{32}H_{42}O_3Si_2$	530			
13	Methyl 2,7,9-tetra chloro-9-H-fluorene-4-carboxylate	$C_{15}H_8Cl_4O_2$	360			
14	9H-Fluorene, 9-Propyl	$C_{16}H_{16}$	208			
15	Methyl benzen	$C_7H_8$	92			
16	Methyl (R)-(-)-3-hydroxy-2-methyl-Propionat	$C_5H_{10}O_3$	118			
17	n-Amyl amine	$C_5H_{13}N$	87			
18	Oxaldihydrazide	$C_2H_6N_4O_2$	118			
19	m-Dioxan	$C_4H_8NO_2$	88			
20	Benzene acetic acid, alpha-acetyl-2,4-dinitro ethyl Ester	$C_{12}H_{12}N_2O_7$	296			
21	1,3-Oxazol	$C_3H_3NO$	69			
22	Hydro cyanic acid	HCN	27	$N \equiv C - OH$		
23	Hydrazin	$N_2H_2$	32	$H_2N - NH_2$		
24	Crotonyl isothiocyanate	$C_5H_5NO_S$	127			
25	Diazo ethan	$C_2H_4N_2$	56	$CH_2 = N = N$		
26	2,4_Dinitrophenyl crotonate	$C_{10}H_8N_2O_6$	252			



As shown in Table 1, adsorbed compounds on aluminosilicagel are the following functional groups: 1) Cyanide, hydrocyanic, azid, nitros amine and nitride groups: important compounds for these groups are Hydro cyanic acid, crotonyl isothiocyanate, diazo ethan , N-nitroso dimethyl amine (DMN) and hydrazin. aluminosilicagel has empty d orbital in silicon structure that has ability to absorb these compounds [Figure 2] . This ability cause Prevention of damage to the lungs, blood alkalinity and damage to body tissues.



**Figure 2:** Empty d orbital of silicon in aluminosilicagel.

2) Poly aromatic hydrocarbons compounds (PAHS): highest adsorption related to poly aromatic hydrocarbons compounds (PAHS) (derivatives of anthracene, phenanthrene, naphthalene, chrysene, fluorene, pyrene and biphenyl). Compounds of these groups that adsorb on aluminosilicagel are: 5H-benzo[def]carbazole, 2-benzyl-4-methyl phenol, 9-(4-tolylamino)Phenanthren, 10-heptyl-10-hydroxy-9(10H)-anthracenone , 2,3-diphenyl quinoxaline , 5H-benzo[def]carbazole, 9-N-dodecyl anthracene, 1,2-epoxy-3,4-dihydroxycyclohexano [a] Perene, methyl 2,7,9,9-tetra chloro-9-H-fluorene-4-carboxylate and 9H-fluorene, 9-propyl. The presence of activated alumina and  $SiO_2$  in aluminosilicagel structure enable it to adsorb aromatic and poly aromatic hydrocarbons via the Reaction between  $\pi$  electrons in aromatics compounds and empty orbitals in alumina and silicon.

## Conclusion

Results of this study show that aluminosilicagel has the ability to absorb amines, cyanides and aldehydes and poly aromatic hydrocarbons compounds (PAHS) and their derivatives in cigarette smoke.

## Experimental

### Material and apparatus

HPLC methanol (MERK), *Equisetum arvense* plant of North of Iran, gas chromatography mass

spectroscopy (GC/MS) SHIMADZO QP2010, Helium gas 99/99% purity, Smoking machine FILTRONA CSM, Shaker GERHARDT LS<sub>2</sub>. Micro silica was extracted with purring obtain silica from equisetum arvense plant ash in 1300 °C in electric furnace at 4 hours. SEM (LEO 1455 VP) in iranian institute for color science and technology (ICPC) analyses was showed a particle size of micro silica in 1-1.5 micrometer (Figure 3). Sodium silicate synthesized from 10 g microsilica and 20 g NaOH in 700 °C in electric furnace for 2 hours and extraction by leaching. Then added 5 mg Al<sub>2</sub>O<sub>3</sub> in sodium silicate solution and mixed in 50 °C and then added HCl until formation of gel. That gel putted in 60 °C for 2 week. After filtration, aluminosilicagel was washed by water and pure methanol and dried in 40 °C. SEM (Figure 4), TEM (Figure 5) and XRD of aluminosilicagel (Figure 6) showed particle size less than 200 nm.

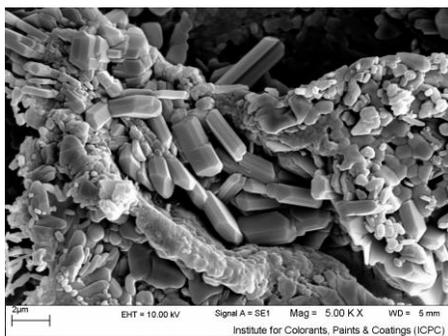


Figure 3: SEM image of Equisetum arvense micro silica

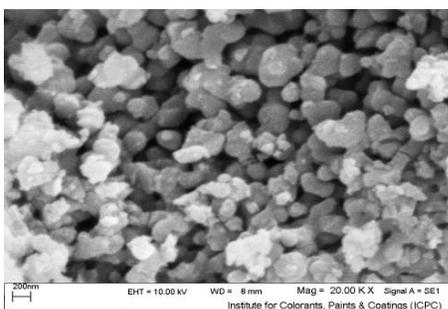


Figure 4: SEM image of aluminosilicagel

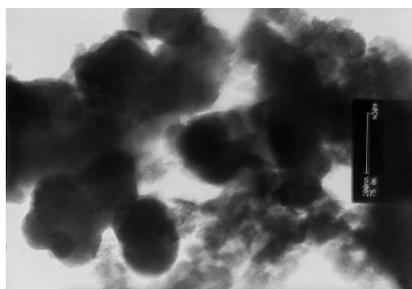


Figure 5: TEM image of aluminosilicagel

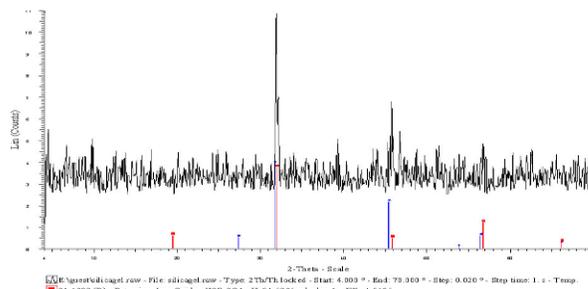


Figure 6. XRD spectrum of aluminosilicagel

Amount of 10 mg aluminosilicagel putted in cigarette filter. Determination of pressure drop was showed 118 mmc. The cigarettes that vehicle of micro silica burned by smoking machine in standard condition. Then aluminosilicagel dispersed in pure methanol and shaker along of 8 hours and 6 degree. Solvents inject to GC/MS after filtration with flowing program and NIST and WILLY229 libraries: Column J&W, DB-5ms. Temperature program : (60°C , for 0.5 min , 250°C at 5°C/min , 250°C for 20 min , 300°C at 30°C/min , 300°C for 7min), oven temperature: 60°C, flow: 0.8 ml/min, Ion source temperature: 200°C, interface temperature: 270°C.

#### Acknowledgements

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