Iranian Journal of Organic Chemistry Vol. 2, No. 3 (2010) 445-449

Identification and removal of amine, cyanide and aldehyde compounds in cigarette smoke via extracted plant's micro silica by gas chromatography – mass spectroscopy (GC/MS) method

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Abstract: Silica is a compound found in some plants and one of the most important materials in chemical industrial and adsorption processes. In this study, micro silica was extracted from *Equisetum arvense* in North of Iran and purified from *Equisetum arvense* plant ash in an electric furnace at 1300°C for 4 hours. SEM measurements determined a particle size of micro silica of 1-1.5 micrometer. The cigarettes used in this study were prepared by adding 5 mg micro silica to each filter tip of the commercial cigarettes. The cigarettes were smoked by machine under standard ISO conditions. The absorbed compounds were extracted by pure methanol and analyzed by GC/MS, using NIST and WILLY229 libraries for identification. Results showed high absorption of amines, nitrosamines, carbamaldehyde, formamide, cyanonitrile and their derivatives. The highest adsorption was found for the following substances: *N,N*-dimehyl formamide, 4-piperidin-1-yl-oxazolidin-2-one, *N*-6-dimethylmalonyl-2-methylpiperidine-1-carbaldehyde, ethylhydrazine oxalate, methylfluoroacetonitrile, ethanediimideic acid dihydrazide, Pyrrole, 2-(hydroxyimino)ethyl acetate, *N*-acetyl-*N*-(acetyloxy) acetamide, methyl phenidate, 2-piperidineneacetic acid, α,α,-phenylmethyl ester, 1-[2-(1,3-cyclopentadien-1-yl)ethyl]pyrolidine, nicotine, *N*-(1-hydroxy-4-oxo-1-phenylperhydroquinolizine-3-yl) carbamic acid benzyl ester, hydrazoic acid, 1-epislaframine, 2-allyl-3,5-dimethylpyrazine, 1-benzoyl-1h-napht[2,3-d]imidazole-6,7-di carboxylic anhydride, propionic amide, ammonium carbamate, L- α -alanine, acetaldehyde, 2-cyanoaziridine, 8-azidoadenosine, tertadecylaldehyde, 1-cyano-1-thioethyl(1′-ethoxy)cyclopentane, nitrosotrimethyleneimine, 4-cyano-4-thioethyl(1′-ethoxy)hepta-1,6-diene, formaldehyde oxime trimer, nitrosomethan amine, 1-(2-methoxy ethyl) hydrazine. This study showed that micro silica due to its acidic structure has the ability to absorb amines, cyanides and aldehydes and their derivatives in cigarette smoke.

Keywords: Micro silica; Gas chromatography mass spectroscopy; *Equisetum arvense* plant; GC/MS method.

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].

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Composition of both gas and particulate phases vary with a broad range of cigarette design features [13]. Important compounds in MCS are PAHS which content 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 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]. Micro silica has ability to adsorb some chemical compound in cigarette smoke. In this study adsorption of amino and cyanide compounds in cigarette mainstream smoke has been investigated.

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_2. 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 **1**). Amount of 5mg micro silica 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 Micro silica 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.

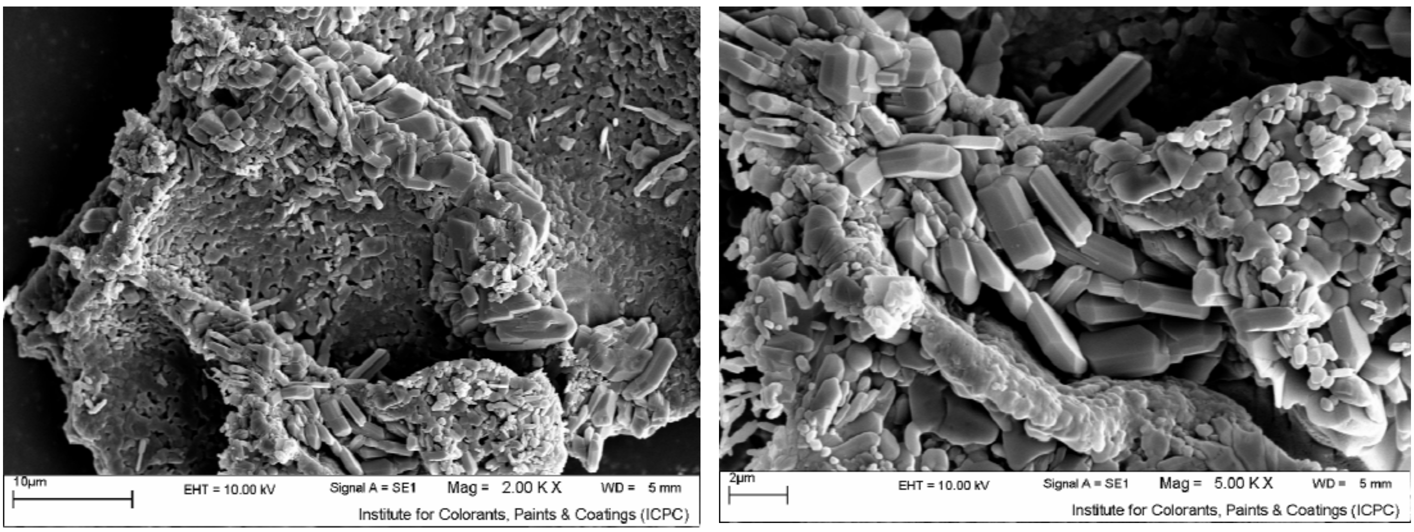


Fig. 1: *Equisetum arvense* micro silica SEM

Results and Discussion

The GC spectrum of cigarette compound adsorbed on *Equisetum arvense* micro silica (diagram **1**) and Mass spectrum were studied. As show in mass spectrum (diagram **1**), the compounds of Table **1** were obtained. Retentions times (R_t) and GC peak areas (p_a) of amine, cyanide and aldehyde compounds in cigarette smoke adsorbed on microsilica and P_a graph comparison adsorbed compounds have been shown in Table **1** and Graph 1, respectively.

Diagram 1. GC spectrum of cigarette compound absorption on Micro silica

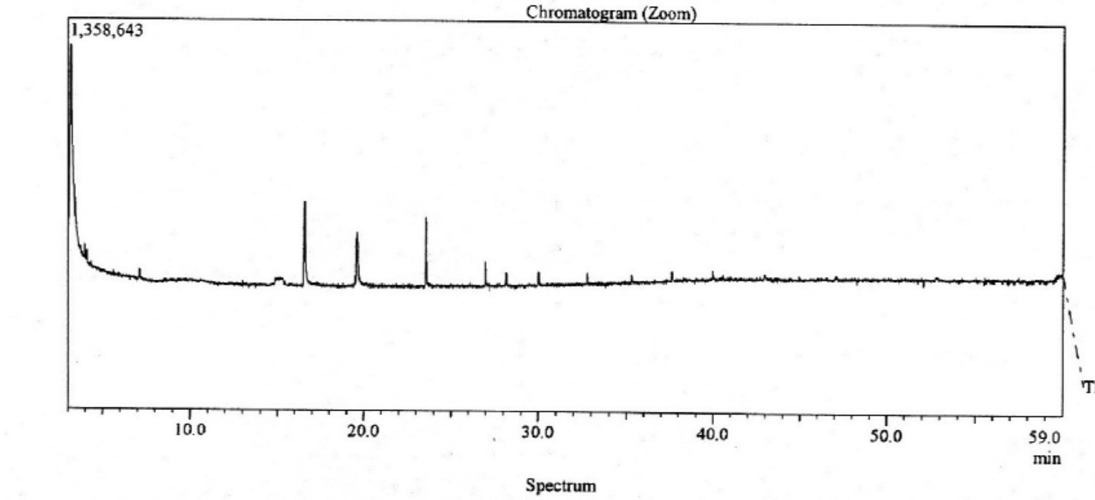
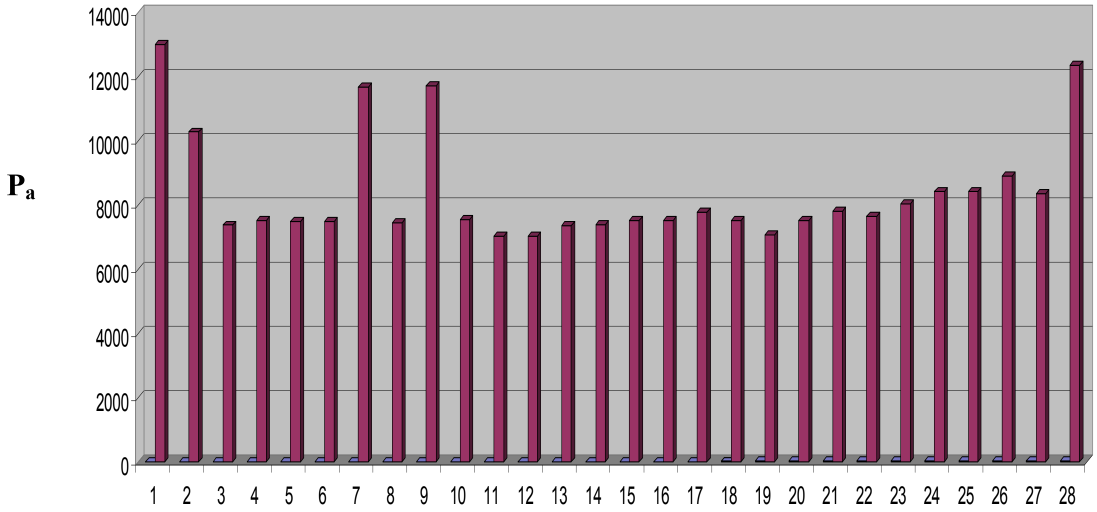


Table 1. Retentions times (R_t) and peak area (p_a) of amine, cyanide and aldehyde compounds adsorbed on micro silica

Entry	Compound names	Formula	R_t	P_a
1	formamide	CH_3NO	3.875	13000.056
2	4- piperidin-1-yl-oxazolidin-2-one	$C_8H_{14}N$	3.142	10273.16
3	4-t-Butyl-2-methoxypiperidine-1-carbaldehyde	$C_{11}H_{21}NO_2$	7.05	7371.504
4	oxamide bis hydrazone	$C_2H_8N_6$	14.7	7509.886
5	anti-2-acetoxyacetaldoxime	$C_4H_7NO_3$	7.075	7485.856
6	*N,N,O*-triacetylhydroxylamine	$C_6H_9NO_4$	7.075	7485.856
7	2-piperidine acetic acid , α -phenyl-,l-ethyl ester	$C_{14}H_{19}NO_2$	16.55	11683.888
8	hydrazoic acid	HN_3	19.217	7465.091
9	1-indolizinol,6-aminooctahydro-9-acetate (ester) , (1. α,6. β,8a. α)-(+-)	$C_{10}H_{18}N_2O_2$	19.267	11711.296
10	7-benzyl-5-vinylidene-7-azabicyclo[4.2.1]nonan-2,8-dion	$C_{17}H_{17}NO_2$	19.426	7540.503
11	*N-P*-bromophenylmaleimide	$C_{10}H_6BrNO_2$	19.442	7035.248
12	benzoel –*H*-napht[2,3-d]imidazole-6,7-dicarboxylic anhydride	$C_{20}H_{10}N_2O_4$	19.467	7025.456
13	Propanamide	C_3H_7NO	21.183	7369.211
14	acetaldehyde	C_2H_4O	21.3	7394.065
15	2-amino-n-ethylpropanamide	$C_5H_{12}N_2O$	26.875	7502.321
16	(+-)-(4.α,5.β.(E))-4-methyl-5-(1-propenyl)-2-imidazolidinon	$C_7H_{12}N_2O$	27.167	7519.61
17	benzeneethanamine,n-[(pentafluorophenyl)methylene]-. β.,3,4-tris[(trimethylsilyl)oxy]	$C_{24}H_{34}F_5NO_3Si_3$	26.942	7758.596
18	2-cyanoaziridine	$C_3H_4N_2$	27.717	7519.049
19	1-oxa-2,5-diazacyclopentadiene	$C_2H_2N_2O$	28.117	7064.608
20	8-azidoadenosine	$C_{10}H_{12}N_8O_4$	28.175	7524.992
21	1-cyano-1-thioethyl(1′-ethoxy)cyclopentane	$C_{10}H_{17}NOS$	30.00	7802.928
22	nitrosotrimethyleneimine	$C_3H_6N_2O$	32.717	7656.188
23	*N*-(2-aminopropanoyl)alanine	$C_6H_{12}N_2O_3$	48.800	8030.834
24	ethyl-7-(3′,5′-dimethylpyrazol-1′-yl)indole-2-carboxylate	$C_{16}H_{17}N_3O_2$	59.658	8410.342
25	*N,N*,2-trimethyl-3-butyn-2-amine	$C_7H_{13}N$	59.667	8425.438
26	1-cyano-1-thioeyhyl(1′-ethoxy)cyclo pentan	$C_{10}H_{17}NOS$	59.725	8905.068
27	thioacetonitrile	C_2H_3NS	59.842	8344.977
28	nicotine	$C_{10}H_{14}N_2$	16.542	12354.954

Graph 1: P_a graph comparison on adsorbed compounds on microsilica



Microsilica for reason to Lewis acid structure has the ability to adsorb carbonyl, amine and cyanide functional groups. Most important amine compounds that have been adsorbed on microsilica were: Formamide, 4-piperidin-1-yl-oxazolidin-2-one, Oxamide bis hydrazone , Anti-2-acetoxyacetaldoxime, *N,N,O*-triacetylhydroxylamine, 2-piperidine acetic acid, α-phenyl-l-ethyl ester, Hydrazoic acid, 1-indolizinol, 6-aminooctahydro-9-acetate(ester), (1. α,6. β,8a.α)-(+-),7-benzyl-5-vinylidene-7-azabicyclo [4.2.1] nonan-2,8-dion,*N-P*-bromophenylmaleimide, Benzoel–*H*-napht[2,3-d]imidazole-6,7-dicarboxylic anhydride, Propanamide, 2-Amino-n-ethylpropanamide, (+-)-(4.α,5.β.(E))-4-methyl-5-(1-propenyl)-2-imidazolidinon, Benzeneethanamine,n-[(pentafluorophenyl)methylene]-.beta.3,4-tris [(trimethylsilyl)oxy], 1-oxa-2,5-diazacyclopentadiene, 8-azidoadenosine, Nitrosotrimethyleneimine, *N*-(2-aminopropanoyl)alanine, Ethyl-7(3′,5′dimethylpyrazol-1′-yl)indole-2-carboxylate, *N,N*,2-trimethyl-3-butyn-2-amine , Thioacetonitrile and Nicotine. Most important cyanide compounds that have been adsorbed on microsilica were: 2-cyanoaziridine and 1-cyano-1-thioeyhyl (1′-ethoxy) cyclopentan. Moreover, most important adsorbed aldehyde compounds were: 4-*t*-Butyl-2-methoxypiperidine-1-carbaldehyde and Acetaldehyde. As shown in Graph **1** highest adsorption on microsilica are related to Formamide, Nicotine, 2-piperidine acetic acid, α –phenyl-,l-ethyl ester, 1-indolizinol,6-aminooctahydro-9-acetate(ester), (1. α,6. β,8a. α)-(+-) and 4-piperidin-1-yl-oxazolidin-2-one. Results of this study showed that micro silica due to its acidic structure has the ability to absorb amines, cyanides and aldehydes and their derivatives in cigarette smoke.

Acknowledgment

We gratefully acknowledge the financial support from the Research Council of Islamic Azad University of Qaemshahr.

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