Asian Journal of Chemistry; Vol. 24, No. 2 (2012), 881-884

ASIAN JOURNAL OF CHEMISTRY

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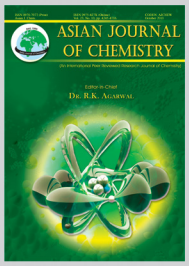

Gas Chromatographic Analysis of Essential Oil Mixture Using Phenyl-Modified Algirian Bentonite

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(*Received*: 25 April 2011; *Accepted*: 19 October 2011) AJC-10551

A new support was prepared from Algerian bentonite by thermal treatment at 1100 ºC and chemically treated by 6N HCl (diameter range 125-150 µm and the surface area S = 12 m^2/g) was grafted by two steps, the first one was a chlorination of the silica surface using dimethyldichlorosilane ($B_{Alg}Cl$) and the second by reacting Grignard reagent with bromophenyl magnesium ($B_{Alg}C_6H_5$), S = 13 m^2/g. The surface properties of octadecyl-modified bentonite were studied by nitrogen adsorption at 77 K. Distinguish the new support with a good stability at high degrees of temperature which enable its application in gas chromatography. Essential oils' mixtures (α- pinene, β- pinene, cineole, fenchone, borneol and anethole) and some fatty acid (C_8, C_{10}, C_{12}, C_{14} and C_{16}) in standard (GLC-30) using the modified $B_{Alg}C_6H_5$ by gas chromatographic analysis were determined. The analytical results were characterized by high precision, accuracy and reproducibility with relative standard deviation not exceeding 2.7 %.

Key Words: Modified Algerian bentonite ($B_{Alg}C_6H_5$), Grignard reagent, Essential oils.

INTRODUCTION

The natural and treated Algerian bentonite were studied using different methods such as chemical analysis, thermal analysis, X-ray diffraction, infrared absorption and nitrogen adsorption to determine their constituents and to characterize the effect of treatment on their superficial structures and textural properties. Results show that the natural bentonite is composed essentially of montmorillonite, quartz and a small quantity of albite. The natural material was thermally treated at 650 and 1100 ºC, then refluxed with 6 N HCl (B_{650} and B_{1100}). The B_{650} sample is composed of quartz, albite, spinel and a small quantity of keatite. The B_{1100} sample is composed of cristobalite, spinel and a small quantity of quartz. The surface areas (S_{BET}) and the total pore volumes are decreased with raising the temperature of thermal treatment (S_{B600} = 160 m^2/g, S_{B650} = 112 m^2/g, S_{B750} = 50 m^2/g, S_{B850} = 24 m^2/g, S_{B950} = 17 m^2/g, S_{B1000} = 13 m^2/g and S_{B1100} = 12 m^2/g)[1].

A support was prepared from Algerian bentonite by thermal treatment at 1100 ºC and chemically by 6 N HCl to remove the soluble metallic oxides especially iron oxide until was obtained white granules with diameter range 125-150 µm. The support specific surface area was measured to be 12 m^2/g. The support granules were silanized with dimethylchlorosilane (DMCS) at 120 ºC in the vapour phase. Determination of different mixtures of normal hydrocarbons C_5 to C_{18} using silanized Algerian bentonite (B_{1100}) as support in gas chromatographic analysis gives high accurate and sensitive results. In all separations of mixtures using columns (200 cm × 2 mm), packed with modified bentonite, the separated peaks with relative standard deviation not exceeding 3.1 % were obtained[2].

Some pharmaceutical compounds such as: butoform, caffeine, menthol, methyl paraben, phenol, propyl paraben and nabumeton were determined using support on the basis of Algerian bentonite in gas chromatographic analysis. The support was prepared by thermal treatment at 1100 ºC and chemically by 6 N HCl (B_{1100}). The B_{1100} granules, with diameter range 125-150 µm and specific surface area 12 m^2/g, were silanized with dimethylchlorosilane (dmcs). The results were characterized by high accuracy and sensitivity with relative standard deviation not exceeding 4.7 %[3].

Two pharmaceutical compounds, phenobarbital and guaifenesine in several commercial pharmaceutical sources were investigated. These compounds were separated using grafted Algerian bentonite (B_{1100}) with SE-52 as support. The compounds were determined by gas chromatography technique. The analytical results show a good precision and reproducibility with a relative standard deviation of 2.8 and 2.9 % for phenobarbital and guaifenesine, respectively[4].

The surface of a chromosorb G (NAW) support (S = 0.5 m^2/g, granules diameters of 250-350 μm) was grafted by two steps, the first one was a chlorination of the silica surface using thionyl chloride ($SOCl_2$) and the second by reacting Grignard reagent with chlorophenyl magnesium. A hybrid surface structure (organic/inorganic) of the chromosorb it had extra characteristics of hydrophobicity. The variation of surface grafted support was realized by plotting the relationship between variation of the logarithm of retention volume and the reverse of absolute temperature log Vs = f (1/T). Distinguish the new support with a good stability at high degrees of temperature which enable its application in gas chromatography. Essential oils' mixtures (α-pinene, β-pinene, cineole, fenchone, borneol and anethole) and some fatty acid (C_8, C_{10}, C_{12}, C_{14} and C_{16}) in standard (GLC-30) and in laurel oil extracted from wild fruit and cultivated laurius nobilis using the modified chromosorb G by gas chromatographic analysis were determined. The analytical results were characterized by high precision, accuracy and reproducibility[5].

Many stationary phases have the general structure shown in Fig. 1. A stationary phase of polydimethyl siloxane, in which all the -R groups are methyl groups ($-CH_3$), is non-polar and often makes a good first choice for a new separation. The order of elution when using polydimethyl siloxane usually follows the boiling points of the solutes, with lower boiling solutes eluting first. Replacing some of the methyl groups with other subsistents increases the stationary phase's polarity, providing greater selectivity; thus, in 50 % methyl, 50 % phenyl, polysiloxane, 50 % of the -R groups are phenyl groups ($-C_6H_5$), producing a slightly polar stationary phase. Increasing polarity is provided by substituting trifluoropropyl ($-C_3H_6CF_3$) and cyanopropyl ($-C_3H_6CN$) functional groups or using a stationary phase based on polyethylene glycol[6-11].

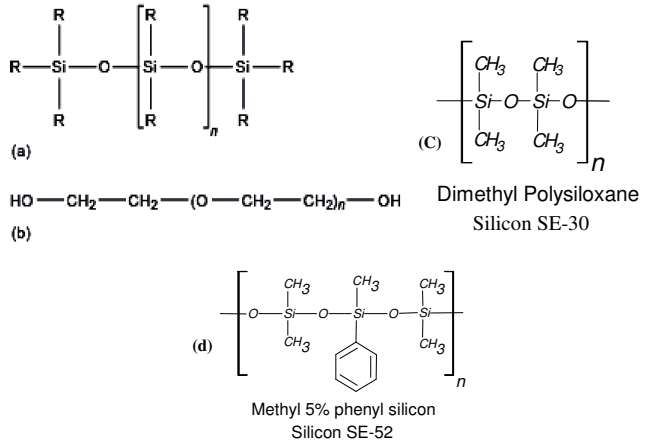


Fig. 1. Many stationary phases: (a) Polydimethyl siloxane; (b) Polyethylene glycol; (c) Dimethyl polysiloxane; (d) Methyl -5 % phenyl polysiloxane

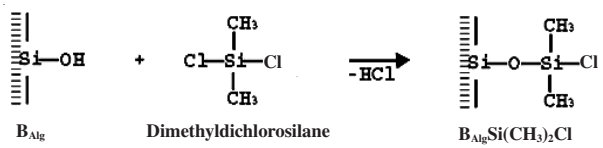
EXPERIMENTAL

Surface area and pore size measurement (BET) were recorded using Micromeritics Gemini III 2375 under nitrogen atmosphere (USA). The chromatograms were obtained by using a GC-9A gas chromatograph equipped with a flame ionization detector (FID) and chromatopac C-R3A printer (Shimadzu Co.), (2 m × 2 mm) stainless steel column, 1 μL syringe (Hamilton Co.), Chromosorb G (NAW) 45- 60 mesh for gas chromatography-Merck, special reactor for grafting. All solvents and chemicals used GR grade.

Essential oils' mixtures (α-pinene, β-pinene, cineole, fenchone, borneol and anethole) and some fatty acid (C_8, C_{10}, C_{12}, C_{14} and C_{16}) in standard (GLC-30).

Preparation of acidic treated bentonite: Bentonite was crushed to obtain small pieces, which have diameter range 125-150 μm, followed by washing with concentrated hydrochloric acid at boiling point for 30 h to remove soluble oxides especially iron oxide. Then it was washed several times with distilled water and dried at 120 ºC for 3 h (B_{Alg}).

Chlorination: 50 g of treated bentonite (B_{Alg}) is dispersed in 250 mL of dichloromethane and 10 mL of dimethyldichlorosilane. The mixture is left under reflux during 2 h. The mixture is evapourated and dried at 280 ºC during 1 h. The chlorinated product was then kept under inert atmosphere of nitrogen ($B_{Alg}Cl$).



Treatment with Grignard reagent: Grignard reagent was prepared by reaction of 15.7 mL of phenyl bromide (RX) with 2.4 g of clean and dry magnesium in 200 mL of anhydrous tetrahydrofuran (THF) according to the reaction:

RX + Mg → RMgX

Organic bromide Magnesium Organomagnesium Br

The chlorinated bentonite ($B_{Alg}Cl$) was added into solution of Grignard reagent under inert atmosphere. The mixture was allowed to reflex for 3 h. Then the heating was removed and contents were allowed to cool. The produce was filtered and washed with methanol and dried at 105 ºC for 2 h ($B_{Alg}C_6H_5$ or $B_{Alg}R$) according the follows:

B_{AlgCl} + RMgX ⟶ $B_{Alg}R$

$B_{Alg}Si(CH_3)_2Cl$ C_6H_5MgBr $B_{Alg}C_6H_5$ or $B_{Alg}Si(CH_3)_2C_6H_5$

RESULTS AND DISCUSSION

Surface properties of B_A and $B_{Alg}C_6H_5$: Surface areas of B_{Alg} and $B_{Alg}C_6H_5$ were determined by the adsorption of nitrogen at 77 K (BET). For determination of properties, the adsorption was carried out until near saturation ($P/P^o \approx 1.0$), then the desorption was completed until closure of the hysteresis loop. Representative adsorption-desorption isotherms of nitrogen for $B_{Alg}C_6H_5$ were studied. The isotherms are II and IV type of SING and BDDT classifications, which indicate the presence of mesoporous structure. Application of the linear BET equation to the nitrogen adsorption data obtained was within the range of relative pressures (0.02-0.25), representation linear BET plots for $B_{Alg}C_6H_5$. From these plots it was found that the BET surface areas (S_{BET}) was 168.25 and 13.0 m^2/g for B_{Alg} and $B_{Alg}C_6H_5$, respectively. The total pore volume v_p (0.440, 0.052 mL/g) were determined from the adsorbed volume at P/Po = 0.95 in the liquid form. The mean pore radii r_a (52.3, 80.0 Å), were determined from the equation: $r_a = 2 \times 10^4 \times v_p/S_{BET}$. The changes of surface area, total pore volume

and mean pore radii during modification can be seen from Table-1. The surface area and the total pore volume decreased from (168.25 m^2/g, 0.440 mL/g) to (13.0 m^2/g, 0.052 mL/g), respectively. The mean pore radii increased from 52.3 to 80.0 Å.

TABLE-1
SURFACE PROPERTIES OF B_{Alg} AND $B_{Alg}C_6H_5$

	S_{BET} (m^2/g)	v_p (mL/g)	r_a (Å)
B_{Alg}	168.25	0.440	52.3
$B_{Alg}C_6H_5$	13.0	0.052	80.0

Hydrophobicity: For the estimation of the changes in the hydrophobicity after modification, we compared dispersibility of the bare and grafted Algerian bentonite in water and benzene. As shown in Fig. 2, the bare Algerian bentonite (B_{Alg}) disperses in the water layer only. Due to the presence of the hydrophobic alkyl groups on the external surface of the $B_{Alg}C_6H_5$ and the hydrophilicity of the rest of the surface, the $B_{Alg}C_6H_5$ was found in organic phase at the benzene-water boundary.

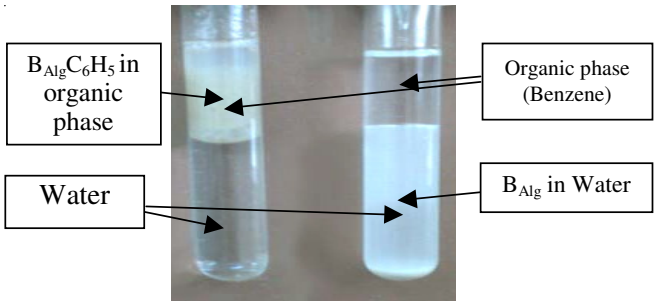


Fig. 2. B_{Alg} in water (right) and $B_{Alg}C_6H_5$ in organic phase (left) dispersed in water/benzene system

Identification of essential oils: The essential oils' mixtures (α-pinene, β-pinene, cineole, fenchone, borneol and anethole), which are using in pharmacologic industries as gastric antiseptics[12] was determined using grafted Algerian bentonite ($B_{Alg}C_6H_5$). The chromatographic conditions for analysis are as the following: analytical stainless steel column (2 m × 2 mm) packed with $B_{Alg}C_6H_5$, programmed column temperature between 35-125 ºC, with increasing temperature rate 6 ºC/min, FID, flow rate of N_2 carrier gas 40 mL/min, the injection volume was 0.2 µL and injected port temperature 175 ºC. A mixture of the six essential oils in a concentration of 0.2 g/5 mL for each one by using the chloroform as solvent (Fig. 3). Fig. 3 shows that the separation was completed with a high precision and reproducibility. The analytical results were characterized by high precision, accuracy and reproducibility (Table-2).

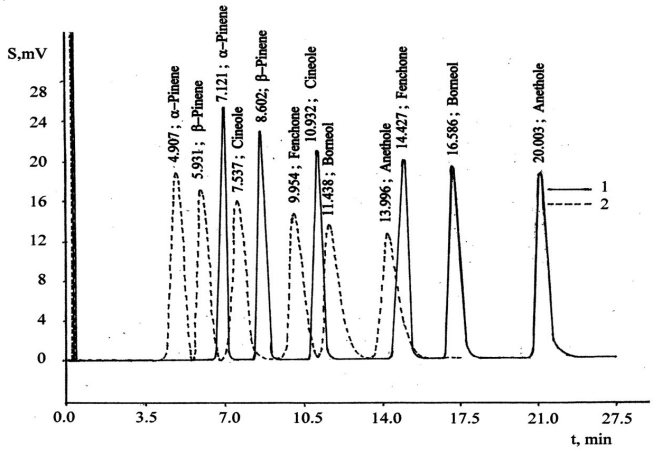


Fig. 3. Chromatogram of mix stander some essential oils using modified $B_{Alg}C_6H_5$ (1) and chromosorb $G.C_6H_5$[5] (2) (column 2 m × 2 mm, programmed temperature 35-125 ºC with increasing rate 6 ºC/min., flow rate of N_2 40 mL/min, the injection volume was 0.2 µL and injected port temperature 175 ºC)

Identification of standard mixture of fatty acids: The fatty acid as methyl esters of a standard mixture containing five components: methyl caprylate, methyl caprate, methyl laurate, methyl myristate, methyl palmitate, by a rate of 20 % from each (GLC-30 Standard Mixtures acc.USP-27) was identified (Fig. 4). These esters were well identified at the determination conditions: analytical stainless steel column (2 m × 2 mm) packed with $B_{Alg}C_6H_5$, programmed column temperature between 90-235 ºC, with increasing temperature rate 6 ºC/min, FID, flow rate of N_2 carrier gas 40 mL/min, the injection volume was 1 µL and injected port temperature 250 ºC. The analytical results were characterized by high precision, accuracy and reproducibility (Table-3).

Tables 2 and 3 (Figs. 3 and 4) show that the use of modified Algerian bentonite ($B_{Alg}C_6H_5$) were better than using a similar column from grafted chromosorb G by phenyl groups ($chromosorb\ G.C_6H_5$)[5].

Conclusion

A new support was prepared from Algerian bentonite by reacting Grignard reagent with bromophenyl magnesium

TABLE -2
DETERMINATION OF MIX STANDER SOME ESSENTIAL OILS ON $B_{Ale}C_6H_5$ COLUMN 2 m × 2 mm, TEMPERATURE PROGRAM (35–125 ºC; 6 ºC/min), N_2 FLOW 40 mL/min, INJECTION PORT TEMPERATURE 175 ºC, V = 0.2 µL

Essential oil	Taken	Amount , V%					
		Found $\overline{m}$ *	RSD (%)	SD	$\frac{SD}{\sqrt{n}}$	$\overline{m} \mp \frac{SD}{\sqrt{n}} \times t$	Recovery (%)
α-Pinene	16.67	16.70	1.62	0.27	0.12	16.70 ± 0.33	100.2
β-Pinene	16.67	16.63	1.65	0.27	0.12	16.63 ± 0.33	99.8
Cineole	16.67	16.67	1.69	0.28	0.13	16.67 ± 0.36	100.0
Fenchone	16.67	16.65	1.73	0.29	0.13	16.65 ± 0.36	99.9
Borneol	16.67	16.68	1.82	0.30	0.13	16.68 ± 0.36	100.1
Anethole	16.67	16.64	1.95	0.32	0.14	16.64 ± 0.39	99.8

*n = 5, t = 2.776

TABLE–3
DETERMINATION OF STANDARD MIXTURE OF FATTY ACID ON $B_{Alg}C_6H_5$ COLUMN 2 m × 2 mm, TEMPERATURE PROGRAM (90–235 ºC; 6 ºC/min) , N_2 FLOW 40 mL/min, INJECTION PORT TEMPERATURE 250 ºC, V = 0.2 µL

Fatty acid	Taken	Amount , V%					
		Found $\overline{m}$ *	RSD (%)	SD	$\frac{SD}{\sqrt{n}}$	$\overline{m} \mp \frac{SD}{\sqrt{n}} \times t$	Recovery (%)
Caprylic acid (C_8)	20.00	20.12	1.94	0.39	0.17	20.12 ± 0.47	100.6
Capric acid (C_{10})	20.00	20.05	1.98	0.40	0.18	20.05 ± 0.50	100.3
Lauric acid (C_{12})	20.00	19.91	2.3	0.46	0.21	19.91 ± 0.58	99.6
Myristic acid (C_{14})	20.00	19.98	2.5	0.50	0.22	19.98 ± 0.61	99.9
Palmitic acid (C_{16})	20.00	19.90	2.7	0.54	0.24	19.90 ± 0.67	99.5

*n = 5, t = 2.776

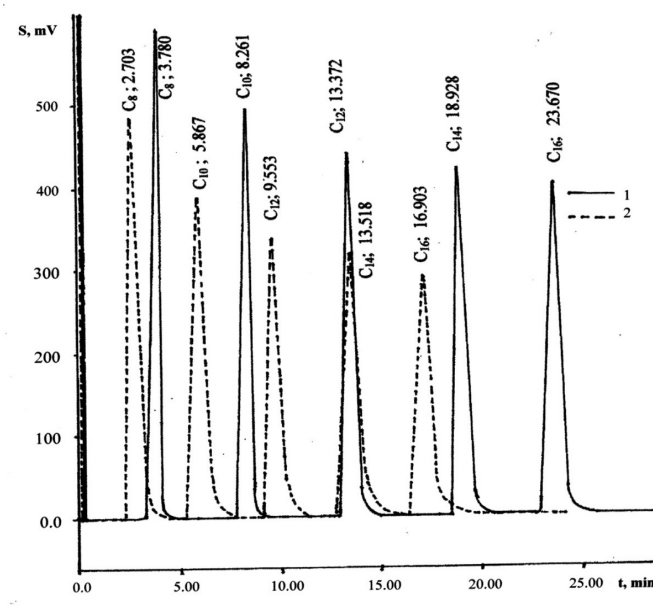


Fig. 4. Chromatogram of standard mixture of fatty acids (C_8, C_{10}, C_{12}, C_{14} and C_{16}) as methyl esters (GLC-30) using modified $B_{Alg}C_6H_5$ (1) and Chromosorb $G.C_6H_5$[5] (2) (column 2 m × 2 mm, programmed temperature 90-235 ºC with increasing rate 6 ºC/min, flow rate of N_2 40 mL/min, the injection volume was 0.2 µL and injected port temperature 250 ºC)

($B_{Alg}C_6H_5$). Distinguish the new support ($B_{Alg}C_6H_5$) with a good stability at high degrees of temperature which enable its application in gas chromatography. Essential oils'mixtures (α-pinene, β-pinene, cineole, fenchone, borneol and anethole) and some fatty acid (C_8, C_{10}, C_{12}, C_{14} and C_{16}) in standard (GLC-30) using the modified $B_{Alg}C_6H_5$ by gas chromatographic analysis were determined. The analytical results were characterized by high precision, accuracy and reproducibility and were better than using a similar column from grafted chromosorb G by phenyl groups (chromosorb $G.C_6H_5$)[5].

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