

Determination of Normal Hydrocarbons C₅-C₁₈ Using Silanized Algerian Bentonite (B₁₁₀₀) as Support in Gas Chromatographic Analysis

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A support was prepared from Algerian Bentonite by thermal treatment at 1100 °C and chemically by 6N HCl to remove the soluble metallic oxides especially iron oxide until we obtained white granules with diameter range 125-150 µm. The support specific surface area was measured to be 12 m²/g. The support granules were silanized with dimethylchlorosilane (DMCS) at 120 °C in the vapour phase. Determination of different mixtures of normal hydrocarbons C₅ to C₁₈ using silanized Algerian Bentonite (B₁₁₀₀) 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.

Key Words: Determination C₅-C₁₈, Bentonite, Support, Gas chromatographic analysis.

INTRODUCTION

Bentonite is considered as a porous cheap material, naturally occurred in Algeria and many parts of the world. It was used in different fields such as refining the mineral oil and edible oil and in the petroleum industry^{1,2}.

Some chromatographic supports are prepared from siliceous or natural origin materials such as diatomaceous earth or Bentonite, which are treated in different ways to deactivate and modify their surface properties. Acid wash treatment by HCl removes all soluble oxides from the surface of the support. Modification of the support surface by silanization with silane compounds or by condensation of a suitable polymer is well reported. Modification of the support surface by reaction with silanol groups was carried out by means of chlorosilane compounds as reactants, or by condensation of a suitable polymer as PEG-20M, SE-30 and OV-101³⁻⁹.

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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 of present study show that the natural Bentonite (NB) is composed essentially of montmorillonite, quartz and a small quantity of albite. The natural material was thermally treated at 650 and 1100 °C then refluxed with 6N HCl (B₆₅₀ and B₁₁₀₀). The B₆₅₀ sample is composed of quartz, albite, spinel and a small quantity of keatite. The B₁₁₀₀ sample is composed of the 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 ($S_{\text{B600}} = 160 \text{ m}^2/\text{g}$, $S_{\text{B650}} = 112 \text{ m}^2/\text{g}$, $S_{\text{B750}} = 50 \text{ m}^2/\text{g}$, $S_{\text{B850}} = 24 \text{ m}^2/\text{g}$, $S_{\text{B950}} = 17 \text{ m}^2/\text{g}$, $S_{\text{B1000}} = 13 \text{ m}^2/\text{g}$ and $S_{\text{B1100}} = 12 \text{ m}^2/\text{g}$)^{10,11}.

Some chromatographic supports from Algerian Bentonite (B₆₅₀ and B₁₁₀₀) were prepared in the diameter range 125-150 microns¹¹⁻¹³. The two above supports granules were modified by silanization with dimethylchlorosilane at 120 °C, under a little flow of nitrogen to avoid dimethylchlorosilane oxidation. A new surface structure possessing dimethylchlorosilane properties was also obtained. A suitable amount of Bentonite granules B₁₁₀₀ ($S = 12 \text{ m}^2/\text{g}$) was modified with Silicone SE-52 at 280 °C. The modification process changed the surface structure of this sample which acquired Silicone SE-52 properties. All columns packed with modified supports participated effectively in separating mixtures of some aromatic and normal hydrocarbons C₅-C₁₂ with fine chromatographic peaks and good reproducibility¹¹⁻¹³.

EXPERIMENTAL

The chromatograms were obtained using a GC-9A gas chromatograph equipped with a flame ionization detector (FID) and chromatopac C-R3A printer (Shimadzu), 1 μL syringe (Hamilton) and special reactor for grafting. All solvents and used chemicals were extra pure grade. Bentonite comes from Roussel quarry, near Maghnia town (northwest of Algeria).

Support preparation

A support was prepared from Algerian Bentonite, by thermal treatment at 1100 °C, then washed with 6N HCl, finally, washed by distilled water until the excess Cl⁻ ions were no longer detectable by the AgNO₃ test. We obtained white Bentonite granules sieved in the diameter range 125-150 μm . The BET specific surface area was measured by N₂ adsorption at 77 K using Gemini Micromeritics III 2375 Surface Area Analyzer USA and was found to be 12 m²/g¹⁰. The support granules were deactivated by silanization with dimethylchlorosilane (DMCS) in the vapour phase at 120°C in presence of dry pure nitrogen stream, then the yield grafted

support was washed by chloroform to remove the residual reagent. The silanized support was dried at 110 °C before being packed in chromatographic column.

The obtained support is used in separating and determining several mixtures of normal hydrocarbon compounds C₅-C₁₈ (pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane and octadecane). Nitrogen was used as carrier gas at flow rate 40 mL/min, injection port temperature: 250 °C, temperature program (120-205 °C; 5 °C/min).

RESULTS AND DISCUSSION

The packed column with DMCS silanized B₁₁₀₀ was suitable for determining and separating mixture of normal hydrocarbons C₅-C₁₈ (Figs. 1-3). In all separations, we obtain completely separated peaks with high sensitivity and reproducibility. The separation time increases from C₅ to C₁₈ (Fig. 4).

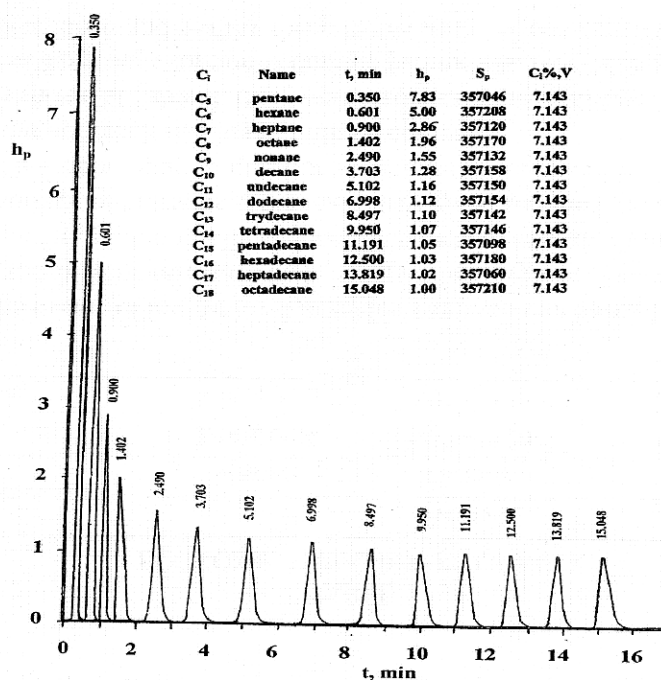


Fig. 1. Separation and determination of first mixture of normal hydrocarbons C₅-C₁₈ (equal per cents) on DMCS silanized B₁₁₀₀ column (200 cm × 2 mm), temperature program (120-205 °C; 5 °C/min), N₂ flow 40 mL/min, injection port temperature 250 °C, V = 0.5 μL

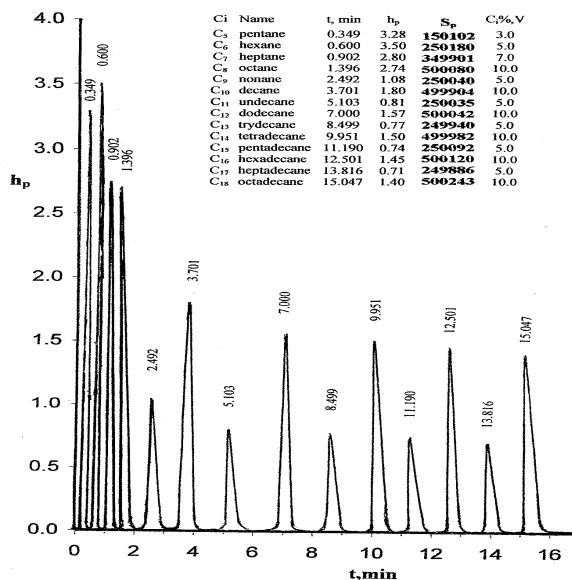


Fig. 2. Separation and determination of second mixture of normal hydrocarbons C₅-C₁₈ on DMCS silanized B₁₁₀₀ column (200 cm × 2 mm), temperature program (120-205 °C; 5 °C/min), N₂ flow 40 mL/min, injection port temperature 250 °C, V = 0.5 μL.

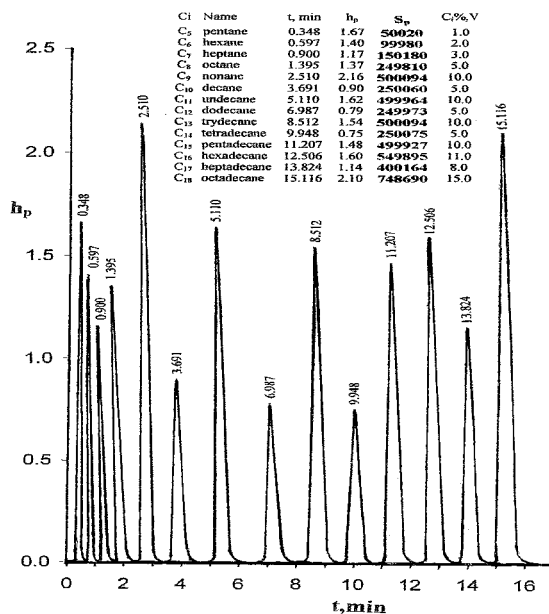


Fig. 3. Separation and determination of third mixture of normal hydrocarbons C₅-C₁₈ on DMCS silanized B₁₁₀₀ column (200 cm × 2 mm), temperature program (120-205 °C; 5 °C/min), N₂ flow 40 mL/min, injection port temperature 250 °C, V = 0.5 μL.

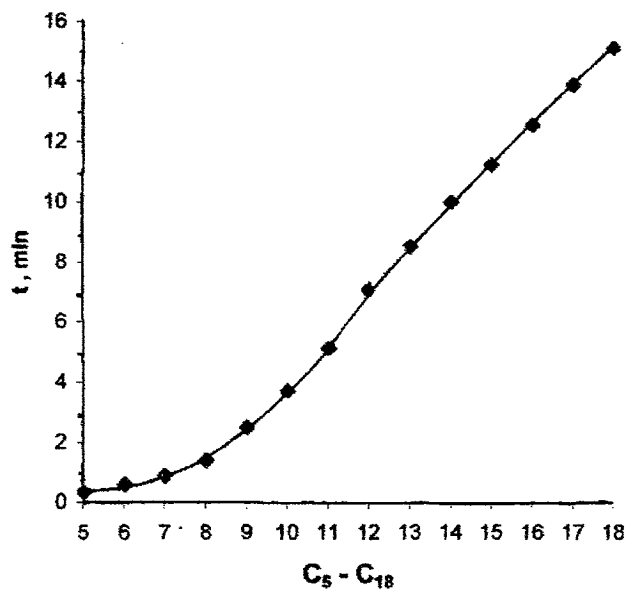


Fig. 4. Separation time (t) of normal hydrocarbons C_5 - C_{18} on DMCS silanized B_{1100} column ($200\text{ cm} \times 2\text{ mm}$), temperature program (120 - $205\text{ }^\circ\text{C}$; $5\text{ }^\circ\text{C}/\text{min}$), N_2 flow $40\text{ mL}/\text{min}$, injection port temperature $250\text{ }^\circ\text{C}$, $V = 0.5\text{ }\mu\text{L}$

The height peak to (h_p) is found sharply decrease from C_5 to C_8 and slowly decrease from C_9 to C_{18} (Fig. 5).

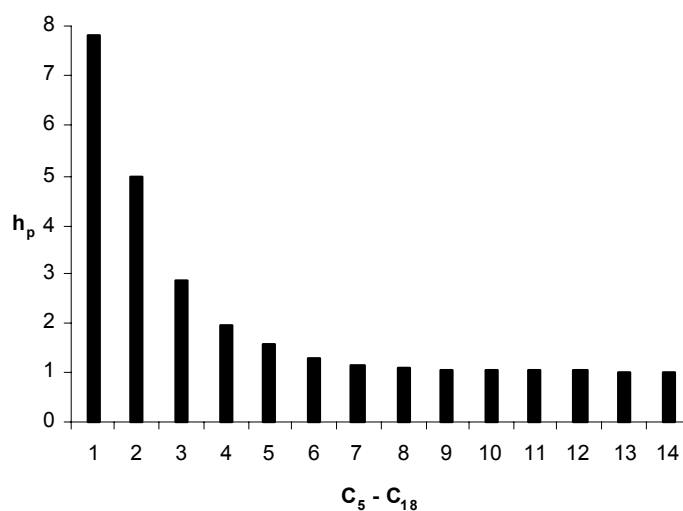


Fig. 5. Height peaks (h_p) of normal hydrocarbons C_5 - C_{18} on DMCS silanized B_{1100} column ($200\text{ cm} \times 2\text{ mm}$), temperature program (120 - $205\text{ }^\circ\text{C}$; $5\text{ }^\circ\text{C}/\text{min}$), N_2 flow $40\text{ mL}/\text{min}$, injection port temperature $250\text{ }^\circ\text{C}$, $V = 0.5\text{ }\mu\text{L}$

Linear calibration curves, $h_p = f(m)$; where: h_p = height of peaks and m = per cent of normal hydrocarbon compounds (C₅-C₁₈) were studied (Fig. 6). These curves showed a linear proportionality.

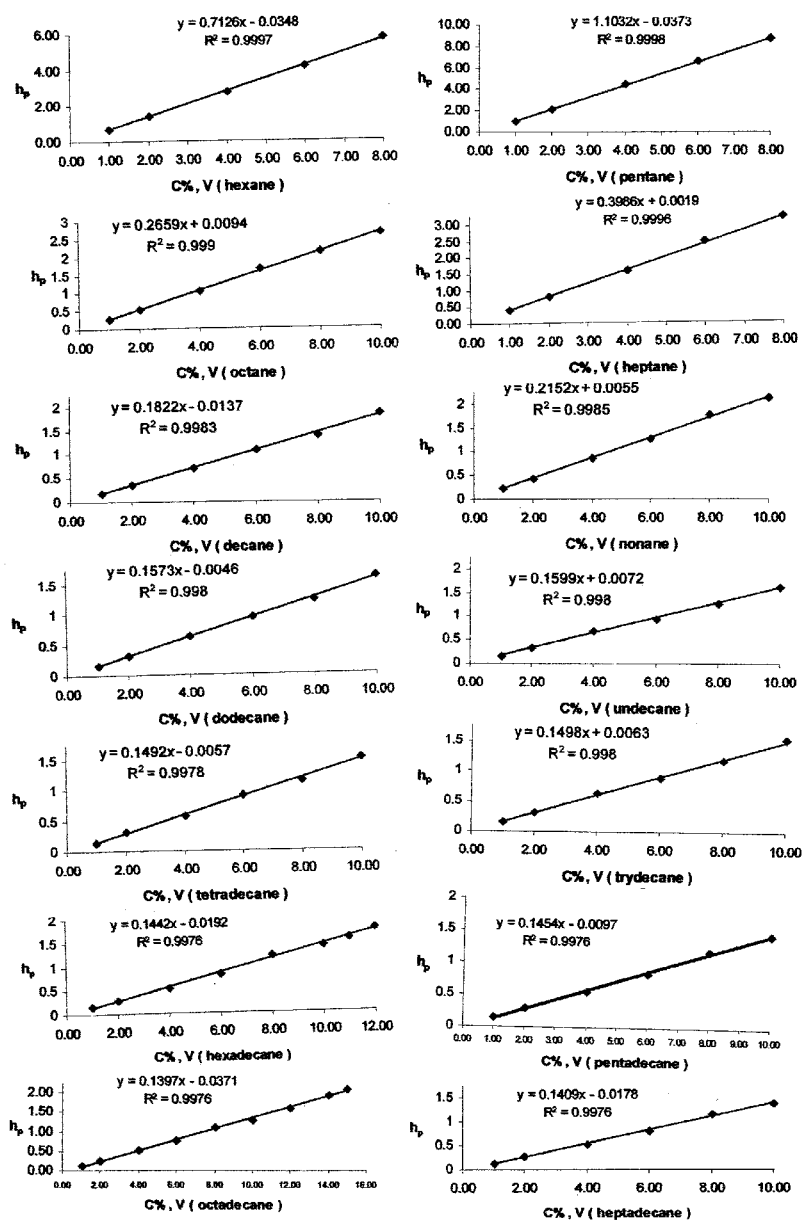


Fig. 6. Linear calibration curves, $h_p = f(m)$ of normal hydrocarbons C₅-C₁₈ on DMCS silanized B₁₁₀₀ column (200 cm × 2 mm), temperature program (120-205 °C; 5 °C/min), N₂ flow 40 mL/min, injection port temperature 250 °C, V = 0.5 μL

Linear calibration curves, $S_{\text{area}} = f(m)$; where: S = area of peak and m = per cent of normal hydrocarbon compounds for the determination of C_5 - C_{18} in the per cent range between 1 to 15 % showed better linear proportionality comparatively with $h_p = f(m)$ curves (Table-1).

TABLE-1
EQUALS OF LINEAR CALIBRATION CURVES, $S_{\text{area}} = f(m)$; WHERE:
 $Y = S_{\text{area}}$, $X = m$ AND m = PER CENT OF NORMAL HYDROCARBON
COMPOUNDS (V) OF NORMAL HYDROCARBONS C_5 - C_{18} ON DMCS
SILANIZED B_{1100} COLUMN (200 cm \times 2 mm), TEMPERATURE
PROGRAM (120-205 °C; 5 °C/min), N_2 FLOW 40 mL/min, INJECTION
PORT TEMPERATURE 250 °C

Normal hydrocarbon compounds	Equals of linear calibration curves	
C_5	$Y = 49887 X + 85.061$	$R^2 = 0.9998$
C_6	$Y = 49920 X + 78.049$	$R^2 = 0.9998$
C_7	$Y = 49934 X + 36.585$	$R^2 = 0.9999$
C_8	$Y = 49947 X + 67.805$	$R^2 = 0.9999$
C_9	$Y = 49950 X + 89.024$	$R^2 \approx 1.0000$
C_{10}	$Y = 49963 X + 26.220$	$R^2 \approx 1.0000$
C_{11}	$Y = 49974 X + 47.560$	$R^2 \approx 1.0000$
C_{12}	$Y = 49954 X + 56.585$	$R^2 \approx 1.0000$
C_{13}	$Y = 49953 X + 92.988$	$R^2 \approx 1.0000$
C_{14}	$Y = 49950 X + 88.720$	$R^2 \approx 1.0000$
C_{15}	$Y = 49946 X + 57.927$	$R^2 \approx 1.0000$
C_{16}	$Y = 49929 X + 89.634$	$R^2 = 0.9999$
C_{17}	$Y = 49925 X + 86.280$	$R^2 = 0.9999$
C_{18}	$Y = 49891 X + 38.415$	$R^2 = 0.9998$

Determination of different mixtures of normal hydrocarbons C_5 to C_{18} gives high accurate and sensitive results. In all separations of mixtures, the completely separated peaks were obtained with relative standard deviation not exceeding 3.1 % (Table-2).

Conclusion

The prepared support DMCS silanized B_{1100} shows good separated peaks in determining the different mixtures of normal hydrocarbons C_5 - C_{18} , with good reproducibility and sensitivity.

TABLE-2
 DETERMINATION OF NORMAL HYDROCARBON COMPOUNDS C₅-C₁₈
 ON DMCS SILANIZED B₁₀₀ COLUMN (200 cm × 2 mm), TEMPERATURE
 PROGRAM (120-205 °C; 5 °C/min), N₂ FLOW 40 mL/min, INJECTION
 PORT TEMPERATURE 250 °C, V = 0.5 µL

No. of mixtures	Compound	C _i	Amount (V %)		
			Taken	Determined	
				\bar{X}	RSD (%)
1	Pentane	C ₅	7.143	7.15	1.26
	Hexane	C ₆	7.143	7.15	1.24
	Heptane	C ₇	7.143	7.14	1.23
	Octane	C ₈	7.143	7.14	1.20
	Nonane	C ₉	7.143	7.13	1.20
	Decane	C ₁₀	7.143	7.15	1.21
	Undecane	C ₁₁	7.143	7.14	1.21
	Dodecane	C ₁₂	7.143	7.14	1.21
	Tridecane	C ₁₃	7.143	7.13	1.22
	Tetradecane	C ₁₄	7.143	7.15	1.23
	Pentadecane	C ₁₅	7.143	7.13	1.25
	Hexadecane	C ₁₆	7.143	7.14	1.26
	Heptadecane	C ₁₇	7.141	7.14	1.28
	Octadecane	C ₁₈	7.143	7.15	1.30
2	Pentane	C ₅	3.00	3.02	2.16
	Hexane	C ₆	5.00	5.01	1.85
	Heptane	C ₇	7.00	6.99	1.47
	Octane	C ₈	10.00	10.02	1.10
	Nonane	C ₉	5.00	5.00	1.39
	Decane	C ₁₀	10.00	9.98	1.02
	Undecane	C ₁₁	5.00	5.01	1.35
	Dodecane	C ₁₂	10.00	10.02	1.08
	Tridecane	C ₁₃	5.00	5.00	1.37
	Tetradecane	C ₁₄	10.00	9.99	1.09
	Pentadecane	C ₁₅	5.00	5.00	1.38
	Hexadecane	C ₁₆	10.00	10.02	1.10
	Heptadecane	C ₁₇	5.00	4.98	1.40
	Octadecane	C ₁₈	10.00	10.02	1.14
3	Pentane	C ₅	1.00	1.01	3.1
	Hexane	C ₆	2.00	2.00	2.45
	Heptane	C ₇	3.00	2.99	2.02
	Octane	C ₈	5.00	4.98	1.36
	Nonane	C ₉	10.00	10.03	0.98
	Decane	C ₁₀	5.00	5.00	1.38
	Undecane	C ₁₁	10.00	9.98	1.12
	Dodecane	C ₁₂	5.00	5.01	1.39
	Tridecane	C ₁₃	10.00	10.00	1.13
	Tetradecane	C ₁₄	5.00	5.00	1.40
	Pentadecane	C ₁₅	10.00	10.02	1.15
	Hexadecane	C ₁₆	11.00	10.99	1.10
	Heptadecane	C ₁₇	8.00	8.01	1.21
	Octadecane	C ₁₈	15.00	14.97	0.95

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