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Preparing a New Support From Octadecyl-Modified Aleppo Bentonite and Using it For Determining of Automobile Gasoline Using Gas Chromatography

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Abstract

A new Octadecyl-modified Aleppo Bentonite support in gas chromatographic analysis (GC) was developed. The method is based on the thermal treatment of Aleppo Bentonite which has diameter particles (150-250 μm) and washed by concentrated HCl (B_A). B_A was chlorinated by dimethyldichlorosilane, then, the resultant product was reacted with Griniard reagent as Octadecylmagnesium bromide to obtain (B_AC_{18}). The surface properties of B_A and B_AC_{18} were characterized by nitrogen adsorption at 77K (BET) and differential thermal analysis (DTA). It was found that the BET surface area (S_{BET}) was 6.67 and 2.50 m^2/g, the total pore volume (V_p) was 0.0164 and 0.0075 mL/g, the mean pores radii (r_a) was 49.175 and 60.0 Å, (V_m) the monolayer capacity was 1.463 and 0.614 ccSTP and constant BET (C_{BET}) was 427.25 and 508.8, respectively. Thirty three hydrocarbons components in gasoline and including separation of benzene (0.771%, where it was not possible to separate it with B_AOctyl) were determined by using B_AC_{18} as support in GC. The principle gasoline components groups (total C_5 to total C_{10}) percent were presented as follows: 18.849%, 10.358%, 38.214%, 10.241%, 15.993% and 3.083% (total C_5-C_{10} =96.738%). The developed support is applied for the determination of some hydrocarbons compounds (as automobile gasoline). The column of B_AC_{18} provided excellent symmetrical peaks and select more compounds compared with B_AOctyl-modified support.

Keywords: Octadecyl-modified Aleppo Bentonite, BET, DTA, GC, Gasoline.

Introduction

Packed columns are widely used at gas chromatographic, which are filled with narrow fractions of either solid adsorbents with a developed surface or solid supports whose surface is coated with a layer of the liquid stationary phase. Mineral solid supports are treated with the vapour of dimethyldichlorosilane or hexamethyldisilazane, which deactivate the hydroxyl groups of the surface. Diatomite supports are used most often and for polar compounds good results are obtained by using inert polymer supports. Aleppo Bentonite is rocky clay which consists of 47% SiO_2, 14.4% Al_2O_3 and some other oxides as Fe_2O_3, MgO, CaO, Na_2O and others [1,2]. The thermal treatment causes decreasing its specific surface area with increasing the temperature [3,4]. Bentonite clays are used in many industrial processes [5,6], and it can be used as chromatographic supports in gas chromatography to separate many mixtures after grafting as: lidocaine hydrochloride, carbinoxamine maleate and chlorphenramine maleate in some pharmaceuticals on grafted Bentonite with silicon OV-1 as support [7]. Bentonite is used also as stationary phase in thin layer chromatography to separate some metal ions and vitamins B_1, B_6, B_{12} [8]. The surface areas (S_{BET}), the mean pores radii (r_a), the total pore volumes (V_p), (V_m) the monolayer capacity and C_{BET} constants of BET were determined [9-11]. Gas chromatographic analysis (GC) of automobile gasoline using phenyl-modified Aleppo Bentonite was studied. The particles of Aleppo Bentonite which have diameter particles (150-250 μm) were thermal treatment and washed by concentrated HCl (B_A). B_A was chlorinated by dimethyldichlorosilane, then, it was reacted with Grignard reagent as phenylmagnesium bromide to obtain (B_APhenyl) [11]. The surface properties of B_A and B_APhenyl were characterized by nitrogen adsorption at 77K and differential thermal analysis (DTA). B_APhenyl was applied to separate thirty nine hydrocarbons components in automobile gasoline in (GC) [11].

A new Octyl-modified Aleppo Bentonite support was developed. B_A was chlorinated by dimethyldichlorosilane, then, the resultant product was reacted with Griniard reagent as Octylmagnesium bromide to obtain (B_AOctyl). The surface properties of B_A and B_AOctyl were characterized by nitrogen adsorption at 77K (BET) and differential thermal analysis (DTA). It was found that the S_{BET}, V_p, r_a, V_m and C_{BET} were 2.71 m^2/g, 0.0072 mL/g, 53.14 Å, 0.620 ccSTP/g and 537.7, respectively (for B_AC_8). Twenty eight hydrocarbons components in gasoline were determined by using B_AOctyl as support by gas chromatographic analysis. The principle gasoline components groups (total C_5 to total C_{10}) percent were presented as follows: 20.265%, 20.691%, 24.383%, 17.110%, 11.595% and 1.611% (95.655%) [12].

In this paper a new support from Octadecyl-modified Aleppo Bentonite (B_AC_{18}) was developed for determination of automobile gasoline using gas chromatographic analysis (GC).

Materials and Methods

Instrumentation

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.), 1 μL syringe (Hamilton Co.). Surface area and pore size measurement (BET) were recorded using Micromeritics Gemini III 2375 under nitrogen atmosphere (USA). Differential thermal analysis (DTA), LINSEIS type STA PT-1600, Germany and pH meter from Radio meter company model Ion Check were used. Diluter pipette model DIP-1 (Shimadzu), having 100 μL sample syringe and five continuously adjustable pipettes covering a volume range from 20 to 5000 μL (model PIPTMAN P, GILSON), an ultrasonic processor model powersonic 405, electronic balance (Sartorius-2474; d=0.01 mg), ash furnace at 100-1200^{o}C type Nabertherm and oven at 50-350^{o}C for treatment Bentonite were used.

Reagents and materials

Tetrahydrofuran, dichloromethane, dimethyldichlorosilane, 1-bromooctadecyl and magnesium metal were purchased from Merck, Germany.

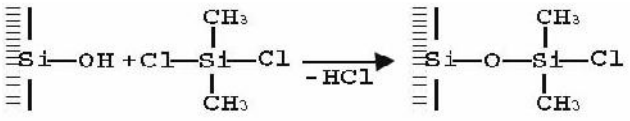
Results and Discussion

Thermal treatment and Acidic washing Bentonite

Bentonite was crushed to obtain small granules, which have diameter particles (150-250 µm), and was thermally treated by two steps at 600°C then at 1000°C, after each step it was refluxed with 6 N HCl at boiling point for 20 hours to remove soluble oxides especially iron oxide. Then it was washed several times with distilled water and dried at 110°C for 3 hours (B_A).

Acid washed Bentonite chlorination

30 g of washed Bentonite (B_A) is dispersed in 250 mL of dichloromethane and 10 mL of dimethyldichlorosilane. The mixture was left under reflux during 3 hours. The solvent was evaporated and the residue was dried at 280°C during 3 hours. The chlorinated product was kept under inert Nitrogen atmosphere (B_ACl), as the equation:

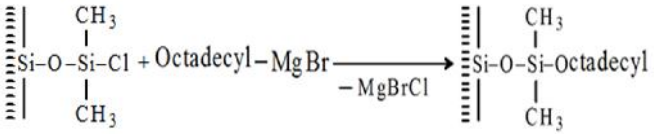


B_A dimethyldichlorosilane B_ACl

Octadecyl-modified Aleppo Bentonite (B_AC_{18})

Grignard reagent was prepared from reaction 34.7 mL of 1-Bromooctadecyl with 2.4 g of clean and dry magnesium in 200 mL of anhydrous tetrahydrofuran (THF) as the equation:

The solution of Grignard reagent was added to chlorinated Bentonite (B_ACl) under inert atmosphere (N_2). The mixture was allowed to reflex for 3h. Then the contents were allowed to cool. The product was filtered and washed with methanol and dried at 110°C for 24 hours (B_AC_{18}), as the equation:



Surface Properties of B_A and B_AC_{18}

Specific Surface areas of B_A and B_AC_{18} were determined by the nitrogen adsorption at 77K (BET) [13-16]. For the determination of textural properties, the adsorption was carried out until near saturation ($p/p_o \cong 1.0$), then the desorption was completed until closure of the hysteresis loop. Representative adsorption-desorption isotherms of nitrogen for B_A and B_AC_{18} are shown in Figure 1. 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 was as the follows:

$$\frac{x}{v_s(1-x)} = \frac{C_{BET}-1}{V_m . C_{BET}} x + \frac{1}{V_m . C_{BET}}$$

$y=m.x+i$; where y is $x/[v_s(1-x)]$, x is p/p_o , v_s is adsorbed volume of N_2, C_{BET} is BET constant and V_m is the monolayer capacity (cc/g STP).

These equations were obtained within the range of relative pressures (0.02 – 0.25) as the follows: $y_1=0.682x+0.0016$ ($R^2=0.9994$) and $y_2=1.625x+0.0032$ ($R^2=0.9996$) for supports B_A and B_AC_{18} respectively.

BET specific surface areas (S_{BET}) were 6.67 and 2.50 m^2/g, the total pores volume V_p were 0.0164 and 0.0075 mL/g (it was determined from the adsorbed volume at p/p_o = 0.95 in the liquid form), the mean pores radii r_a were 49.175 and

60.00 Å (it was determined from the equation: $r_a = 2.10^4.V_p/S_{BET}$), V_m the monolayer capacity were 1.463 and 0.614, cc/g STP and C_{BET} constants of BET were 427.25 and 508.80, for supports B_A and B_AC_{18} respectively. The variation of specific surface area (S_{BET}, m^2/g), total pores volumes (V_p, mL/g), mean pores radii (r_a, Å) and (C_{BET}) causing by grafting modification, as seen in Table 1.

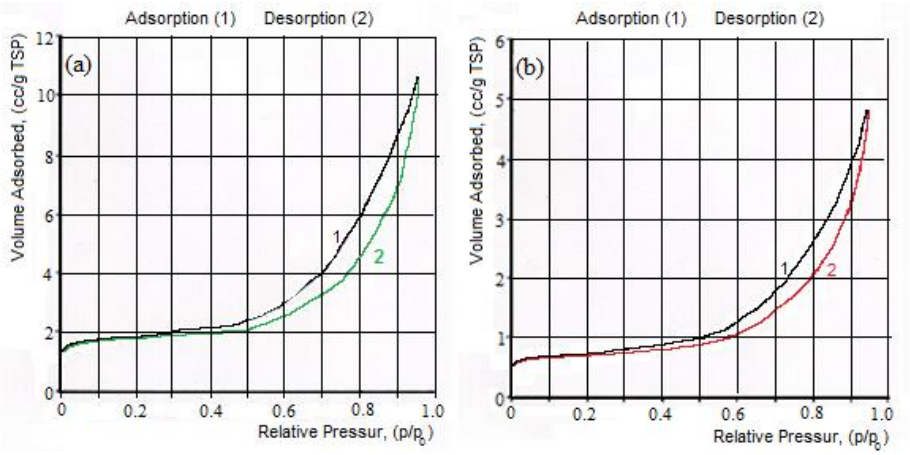


Fig. 1. Adsorption-desorption isotherm of nitrogen at 77K on B_A(a) and on B_AC_{18} (b).

Table 1: Surface properties of B_A and B_AC_{18}.

Support	S_{BET}, m^2/g	V_p, mL/g	r_a, Å	V_m, ccSTP/g	C_{BET}
B_A	6.67	0.0164	49.175	1.463	427.25
B_AC_{18}	2.50	0.0075	60.00	0.614	508.8
B_AOctyl [12]	2.71	0.0072	53.14	0.620	537.7
B_APhenyl [11]	4.21	0.0155	73.49	0.963	357.9

It was noticed that the specific surface area and the total pores volume for B_A and B_AC_{18} decreased from (6.67 m^2/g and 0.0164 mL/g) to (2.50 m^2/g and 0.0075 mL/g) and the mean pores radii increased from 49.175 Å to 60.00 Å, respectively.

In comparison with B_APhenyl-modified column [11], it was found that the S_{BET}, V_p, r_a values and V_m of B_AC_{18} modified column decreased from 4.21 m^2/g, 0.0155 mL/g, 73.49 Å and 0.963 ccSTP/g to 2.50 m^2/g, 0.0075 mL/g, 60.00 Å and 0.614 ccSTP/g, and C_{BET} values increased from 357.9 to 508.8, see Table 1.

Differential Thermal Analysis (DTA):

A useful method for the characterization of B_A and B_AC_{18} was measured by differential thermal analysis (DTA) technique [17-19] in air atmosphere using 40 mg Bentonite with α-Al_2O_3 as reference and heating rate 10^oC/min. Figure 2 shows that, the DTA trace of the B_A and B_AC_{18}. It exhibited two endothermic peaks. The first appears at 145^oC, which is corresponding to the loss of water of hydration. The second, which occurred at about 612^oC, is related to the burning of hydrocarbon in B_AC_{18} support.

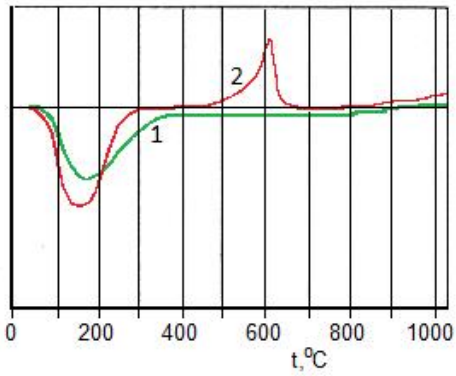


Fig. 2. Differential thermal analysis curve for B_A (1) and B_AC_{18} (2) (in air atmosphere using 40 mg bentonite with α-Al_2O_3 as reference and heating rate 10°C/min).

Hydrophobicity

Hydrophobicity estimation before and after modification, by comparing the dispersiblility of the B_A and B_AC_{18} in water and n-hexane [20,21]. Figure 3 showed that the B_A dispersing was in water layer only. By opposition, the presence of hydrophobic alkyl group on the external surface of B_AC_{18}, made the B_AC_{18} deposited in organic phase at the n-hexane-water.

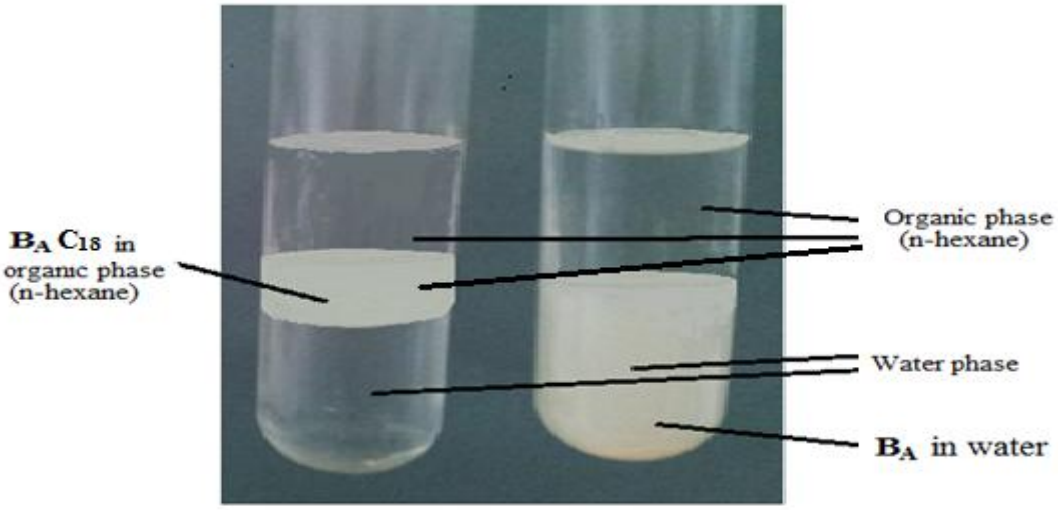


Fig. 3 . B_A (right) and B_AC_{18} (left) dispersed in water/ n-hexane (organic phase) system.

Variation of the logarithm of retention volume in function of the reverse of absolute temperature log v_s=f(1/T)

The modification superficial structure of Octadecyl-modified Aleppo Bentonite (B_AC_{18}) compared to bare one B_A was studied by "inverse gas chromatographic method" in the range 50-110°C and column dimension (100 cm × 4 mm) using dichloromethane (polar), benzene (moderate polarity) and *n*-pentane (non-polar) as auxiliary solutes. The plotted relationship log v_s=f(1/T) showed that, a decreasing of volume retention was noticed with grafted Bentonite by modification Octadecyl group compared to bare B_A, see Figure 4. This figure also shows that the three auxiliary solutes approve the modification of the superficial structure of the Bentonite B_A support surface.

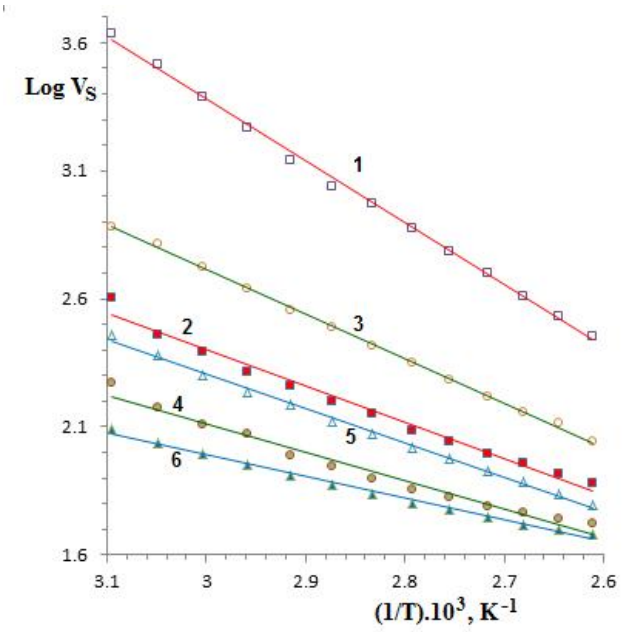


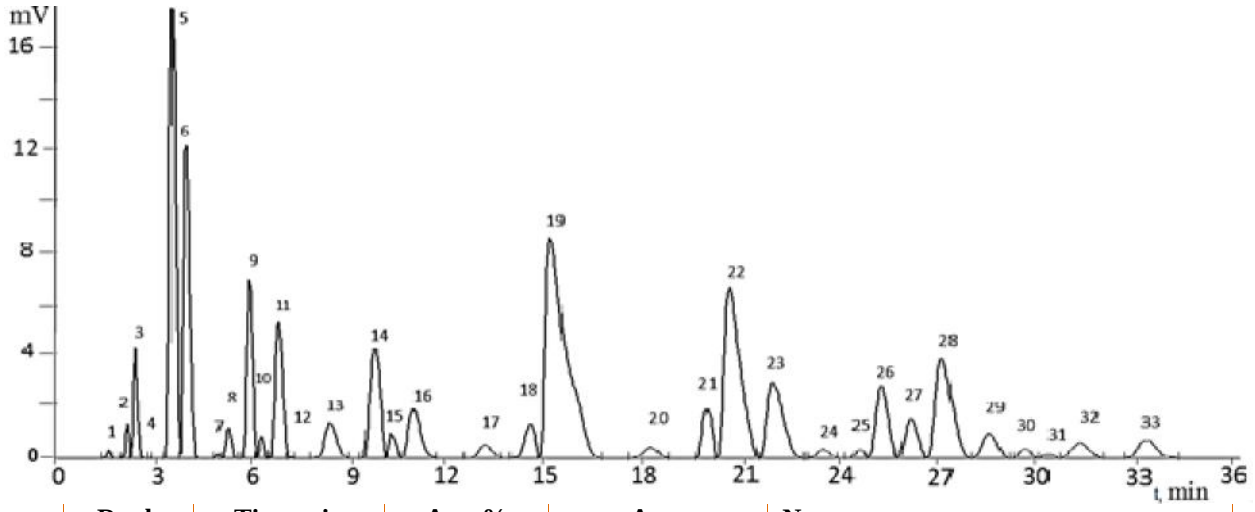
Fig. 4. Variation of log Vs = f(1/T) on (100 cm × 4 mm) packed columns using bare Bentonite B_A (1, 3, 5) and Octadecyl-modified Aleppo Bentonite B_AC_{18} (2, 4, 6); benzene (1, 2); dichloromethane (3, 4); *n*-pentane (5, 6).

Identification of automobile gasoline

Select the automobile gasoline to test for the validity of the B_AC_{18} support and compare its results with the Phenyl-modified Aleppo Bentonite (B_APhenyl) [11] and Octadecyl-modified Aleppo Bentonite (B_AOctyl) [12] as support. This method has been developed for the determination of gasoline components by gas chromatography with flame ionization detector (FID) using Octadecyl-modified Aleppo Bentonite (B_AC_{18}) as support. The chromatographic conditions for analysis are as the following: analytical copper column (100 cm × 4 mm), packed with B_AC_{18}, programmed column temperature between 42-160ºC, with increasing temperature rate 3ºC/min, FID, flow rate of N_2 carrier gas 35 mL/min, the injection volume 0.5 µL and injected port temperature 190ºC. Thirty three hydrocarbons components in gasoline and including separation of benzene (0.771%, where it was not possible to separate it with B_AOctyl) were determined by using B_AC_{18} as support in GC. The gasoline chromatogram was shown in Figure 5. The components groups (C_5 –C_{10}) of gasoline were observed in Table 2.

Table 2: Carbon Number of components groups in automobile gasoline by GC analysis using Octadecyl - modified Aleppo Bentonite (B_AC_{18}).

Carbon number (Identity)	Amount
Total C_3	0.176%
Total C_4	2.428%
Total C_5	18.849%
Total C_6	10.358%
Total C_7	38.214%
Total C_8	10.241%
Total C_9	15.993%
Total C_{10}	3.083%
Total C_3-C_{10}	**99.342%**
Total C_5-C_{10}	**96.738%**



Rank	Time,min	Area%	Area	Name
1	1.603	0.1759	3579	n-Propane
2	2.127	0.471	9584	Isobutane
3	2.384	1.957	39835	n-Butane
4	2.867	0.01921	391	Unknown
5	3.518	9.749	198396	Isopentane
6	3.930	8.346	169838	n-Pentane
7	4.956	0.08083	1645	Unknown
8	5.206	0.7545	15354	2-Methyl butane
9	5.906	4.699	95633	2,3-Dimethyl butane
10	6.265	0.475	9667	Iso hexane
11	6.742	4.413	89807	n-Hexane
12	7.247	0.03951	804	2-Methyl hexane
13	8.309	1.911	38891	3-Methyl hexane
14	9.721	4.764	96954	Isoheptane
15	10.198	0.771	15690	Benzene
16	10.882	2.375	48327	n-Heptane
17	13.057	0.909	18499	2,2-Dimethyl pentane
18	14.501	1.569	31939	2,3,4-Trimethyl pentane
19	15.056	18.19	370134	Toluene + n-Octane
20	18.157	0.8237	16762	2,3-Dimethyl hexane
21	19.855	1.839	37420	2-Methyl octane
22	20.517	11.59	235848	Ethyl benzene
23	21.806	5.291	107683	o-Xylene
24	23.344	0.6166	12547	p-Xylene
25	24.595	0.3769	7669	m-Xylene
26	25.153	3.824	77826	1-Methyl-3-ethyl benzene
27	26.032	2.09	42527	1,2, 4-Trimethyl benzene
28	27.019	6.619	134692	1,2, 3-Trimethyl benzene
29	28.454	1.621	32980	1,3,6-Trimethyl benzene
30	29.562	0.5577	11350	Unknown
31	30.195	0.2613	5317	1,4-Dimethyl-2-ethyl benzene
32	31.258	1.3	26462	1,4-Diethyl benzene
33	33.295	1.522	30977	Diethyl benzene
Total		100	2035027	

Fig.5. Gas chromatographic analysis of automobile gasoline components using grafted Aleppo bentonite B_AC_{18} (Programmed column temperature between 42-160ºC, with increasing temperature rate 3ºC/min, FID, flow rate of N_2 carrier gas 35 mL/min, the injection volume 0.5 µL and injected port temperature 190ºC).

Conclusion

Octadecyl-modified Aleppo Bentonite (B_AC_{18}) as support for GC was developed. The BET surface area (S_{BET}) for this support, the total pores volume (V_p), the mean pores radii (r_a), (V_m) the monolayer capacity, and C_{BET} constant of BET were 2.50 m^2/g, 0.0075 mL/g, 60.00 Å, 0.614, cc/g STP and 508.8, respectively. Thirty three hydrocarbons components in automobile gasoline and including separation of benzene (0.771%, where it was not possible to separate it with B_AOctyl) were determined by using B_AC_{18} as support in GC. The principle automobile gasoline components groups (total C_5 to C_{10}) were presented as follows: 18.849%, 10.358%, 38.214%, 10.241%, 15.993% and 3.083% (total C_5-C_{10} = 96.738%).

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