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Fullerene C_{60} as a New Stationary Phase in Capillary Gas Chromatography

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For the first time, fullerene C_{60} has been used in capillary gas chromatography and its ability towards dispersive interactions has been measured; a C_{60} column has potential in the analysis of organic compounds.

Fullerenes were discovered in 1985[1], among them organic-soluble fullerene C_{60}, a spherical conjugated species with 20 hexagonal and 12 pentagonal rings of carbon atoms. The length of the bonds in the hexagonal and pentagonal rings are 1.4 and 1.45 Å, respectively, and the molecular diameter of C_{60} is 7.1 Å.[2] In the solid state the C_{60} spheres pack together into approximately close-packed lattices.[3] In such lattices the orientation of the neighbouring C_{60} molecules is arranged so as to maximize the intermolecular interactions between surface carbon atoms in adjacent pentagons.[4] Delocalization of electronic charge within and between the extended orbitals of the C_{60} icosahedra is of central importance in understanding its physical properties in the condensed phase.[3]

Fullerene C_{60} is a very stable substance. It is not oxidized at 450 °C in an atmosphere of 25% oxygen with argon, and a sample of C_{60} substantially sublimes between 550–600 °C.[5] Fullerene C_{60} is the softest of the solid carbon forms.[6]

The chemical properties of C_{60} can be compared with electron-deficient arenes.[7,8] In our opinion such properties of C_{60} as the spherical form of the molecule, thermostability, ability to exhibit donor-acceptor interactions and high regularity in the solid state are very promising for gas chromatography (GC). An investigation of fullerene C_{60} as a stationary phase in GC is therefore very interesting in both practice and in theory. A comparison of the ability of C_{60} to exhibit dispersive interactions with graphitized carbon black and apolar liquid stationary phases, measured by the free-energy methylene unit sorption $\Delta G(CH_2)$ of n-alkanes, should allow us to determine the advantages and specifity of C_{60}.

In this paper, for the first time, fullerene C_{60} was used as a stationary phase in GC. A mixture of C_{60}:C_{70} (90:10) was obtained according the method given in ref. 2. C_{60} was isolated by vacuum fraction sublimation from the mixture C_{60}:C_{70}. The purity of C_{60} (99.9%) was confirmed by UV/VIS spectra, bands 328 nm, 540 nm and shoulder 404 nm.[9] The bands for C_{70} 362, 380 and 470 nm were absent in the spectra of C_{60}. The capillary glass column (15 m × 0.29 mm) was coated with fullerene C_{60} using the high-pressure static method.[10] The film thickness of the fullerene was 0.1 μm. The internal surface of the glass capillary column had a very nice golden colour.

GC analyses on a column with C_{60} were carried out on a chromatograph with flame-ionization detector. The temperture of the injector and detector was 200 °C. At isothermal analysis the temperature of the column was 130 and 170 °C. We also analysed substances with the temperature programmed from 130–200 °C at the rate 6 °C min^{-1} and from 110–150 °C at the rate 8 °C min^{-1}.

The helium carrier gas flow splitting ratio was 1:30 and injected sample volumes were 0.1–0.4 μl. n-Alkanes C_8–C_{19} and the organic substances given in Table 1 were used as test compounds. The higher fatty acid methyl esters of Antarctic krill E.superba were also analysed.

Fig. 1 shows that n-alkanes eluate symmetrical peaks from a column with C_{60} according to their boiling points. It can be seen

Table 1 Boiling points[10] and retention indices of test compounds on the column with fullerene.[a]

Compound	Boiling point/°C	Retention indices
1 *o*-Anisidine[b]	225	1092
2 *N,N*-Dimethyldodecylamine	233–234	1393
3 Diphenylamine	302	1525
4 *N*-Octylaniline	177–178/25 mm	1630
5 *m*-Cresol[c]	203	1120
6 Undecanol	146/30 mm	1254
7 β-Naphthol	285–286	1556
8 β-Naphthylamine	306	1475
9 Hexachlorobenzene	332	1598
10 Naphthalene	218	1135
11 Anthracene	340	—

[a] No. of theoretical plates calculated from *N*-octylaniline at 130 °C, 53516. [b] 1–4, Kovats indices at 130 °C. [c] 5–10, indices at programmed temperature from 110–150 °C at the rate 8 °C min $^{-1}$.

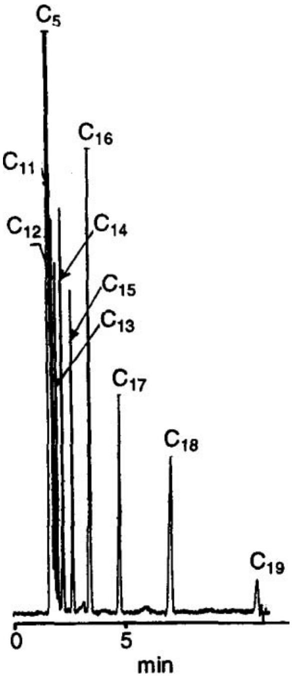

Fig. 1 Chromatogram of n-alkanes C_{11}–C_{19} on a glass capillary column with fullerene C_{60} at 130 °C, sample volume 0.1 µl of pentane solution.

that the first peak separated from the solvent is undecane (b.p. 196 °C). Nonadecane, b.p. 330 °C, elutes after 11 min. Thus, the column with C_{60} may be used for isothermic analysis of high-boiling hydrocarbons at 130 °C.

To estimate the ability of C_{60} to exhibit dispersive interactions with different analytes the energy contribution of the methylene unit $\Delta G(CH_2)$ of n-alkanes was calculated by equation (1),[11]

$$\Delta G(CH_2)_{n,n-1} = -RT\ln(t'_n/t'_{n-1}) \qquad (1)$$

where t'_n and t'_{n-1} are the adjusted retention times of n-alkanes with n and $n-1$ carbon atoms in the molecules, respectively, R is the universal gas constant and T is the column temperature in K. The results are given in Table 2. As one can see, the value of $\Delta G(CH_2)$ on the column with fullerene is comparable with liquid SP of Apiezon L and Squalane[12] and less than twice those for the solid carbon sorbents.[13,14] This means that fullerene C_{60} is analogous to the apolar liquid phases in its ability to exhibit dispersive interactions. This fact is unusual and very interesting. We probably have a variant of 'liquid' GC, but not sorption GC; this may help in understanding the nature of Van der Waals interactions in GC.

Table 2 Free energy of sorption of methylene unit $\Delta G(CH_2)$ of n-alkanes in GC.

Phase	$-\Delta G(CH_2)$ /J mol^{-1}	Analysis temperature/°C
Fullerene C_{60}	2018	100
Apiezon L	2124	120
Squalane	2179	120
Non-porous acetylene soot, modified by pyrocarbon (Carbochrom AC)[a]	4914	100
Graphitized thermal carbon black[a]	4511	100

[a] $\Delta G(CH_2)$ were calculated by us from refs. 13 and 14.

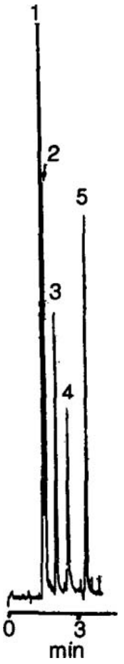

Fig. 2 Chromatogram of amines on a glass capillary column with fullerene C_{60} at 130 °C, sample volume 0.4 µl of ether solution. 1, Diethyl ether; 2, *o*-anisidine; 3, *N,N*-dimethyldodecylamine; 4, diphenylamine; 5, *N*-octylaniline.

We analysed on a C_{60}-column high-boiling organic compounds with different functional groups. The primary, secondary and tertiary amines eluted symmetric peaks according to their boiling points; this is unusual for apolar liquid stationary phases (Fig. 2). The time for amine analysis was only 4 min.

In Fig. 3 the chromatograms of undecan-l-ol, benzenes and naphthalenes with different functional groups are given and retention indices at a programmed temperature calculated by the formula in ref. 15 are given in Table 1. Hexachlorobenzene, b.p. 332 °C. [no. 7, Fig.3 (*a*)] eluted a symmetrical peak after 5.6 min. Tailing was observed only for substances with an OH-group. β-Naphthol, b.p. 285 °C, emerged from the column later than β-naphthylamine with b.p. 306 °C. Thus, the presence of the OH-group in the analyte caused the tailing of peaks due to donor-acceptor interactions with fullerene. The peak broadening of anthracene may be explained by the donor-acceptor interaction of anthracene with C_{60}.[7] However, as seen from Fig. 3(*b*), an increase in analysis temperature to 170 °C allowed the obtention of symmetrical peaks from these compounds because of the low energy of the donor-acceptor interaction with C_{60}. This means that donor-acceptor interaction of C_{60} with arenes and OH-containing compounds are very sensitive to temperature.

To investigate the ability of C_{60} to conduct analyses of complex mixtures we chose the higher fatty acid methyl esters of

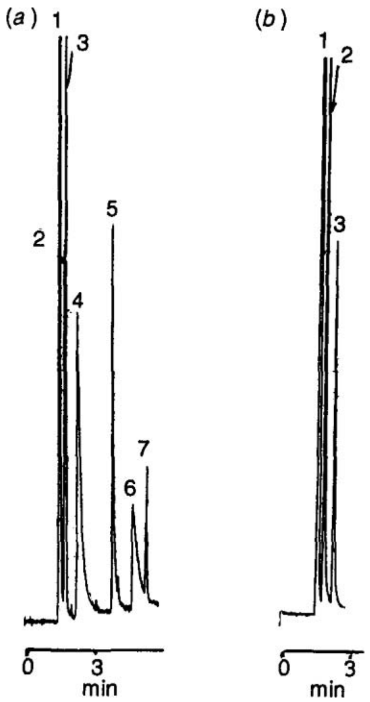

Fig. 3 Chromatograms of organic compounds on a glass capillary column with fullerene C_{60}. (*a*) Programmed temperature 110 °C (2 min), 8 °C min^{-1}, 150 °C, sample volume 0.4 µl of ether solution. 1, Diethyl ether; 2, *m*-cresol; 3, naphthalene; 4, undecan-l-ol; 5, β-naphthylamine; 6, β-naphthol; 7, hexachlorobenzene. (*b*) Temperature of analysis 170 °C, sample volume 0.2 µl of benzene solution. 1, Benzene; 2, β-naphthol; 3, anthracene.

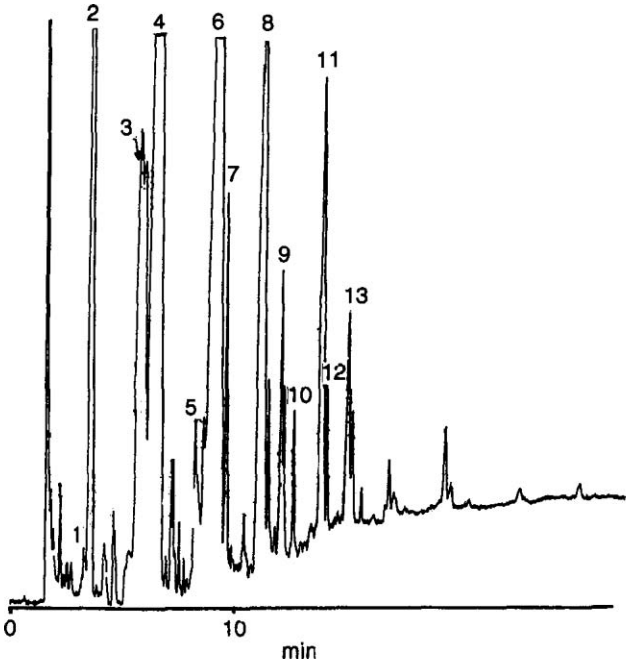

Fig. 4 Chromatogram of methyl esters of fatty acids Antarctic krill E. superba on a glass capillary column with fullerene C_{60} at programmed temperature 130 °C (2 min), 6 °C min^{-1}, 200 °C, sample volume 0.1 µl of pentane solution. 1, 14:1; 2, 14:0; 3, 16:1ω7, 16:1ω9, 4, 16:0; 5, 18:4ω3; 6, 18:1, 18:2ω6, 18:3ω3; 7, 18:0; 8, 20:4ω6, 20:5ω3; 9, 20:1ω9, 20:1ω7; 10, 20:0; 11, 22:6ω3; 12, 22:5ω3; 13, 22:1.

Antarctic krill E. Superba. The separation was carried out at a programmed oven temperature from 130 °C at 6 °C min^{-1} to 200 °C. The methyl esters of C_{18} fatty acids eluted in 10 min under our conditions. There was no resolution of unsaturated esters. The elution time of these compounds on a fullerene column is 3.6 times less than on the non-polar DB-Wax column.[16]

The column has been used extensively over a period of 2 months and no significant changes in retention and selectivity have been observed.

The results show that the fullerene C_{60} can be used as the stationary phase in capillary GC for rapid analyses of high-boiling organic compounds: aromatic and aliphatic hydrocarbons, amines, alcohols and esters. A capillary column with C_{60} is very promising for GC-MS analysis because of the high thermostability of C_{60}. Capillary columns with C_{60} show significant potential in GC.

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