

Extraction of C₆₀ from fullerene-containing carbon soots

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Extraction of fullerene-containing carbon soots with various organic solvents has been studied at room temperature. Yields and compositions of toluene-soluble carbon soot fractions have been determined. Extracts of different carbon soot samples treated according to the toluene—trichlorobenzene—nitrobenzene scheme are studied.

Key words: carbon soot, fullerenes, extraction.

Recently discovered modifications of carbon,^{1,2} fullerenes, are of considerable interest to researchers. Methods for synthesizing fullerenes are presently being actively developed, and their properties are under study.^{3,4}

In our previous report,⁵ the effect of various parameters of an electric arc on the yield of fullerenes was analyzed, and the setup, which allows one to obtain carbon soot with a 20 to 40% content of fullerenes, was described. As a rule, fullerenes can be prepared by the electric arc method in three stages: (1) synthesis of the fullerene-containing soot; (2) extraction of fullerenes from the fullerene-containing soot; and (3) separation and purification of fullerenes.

It is important to correctly choose conditions of extraction of fullerenes for optimizing the synthesis of fullerene-containing soots, because the yield and composition of an extract depend on the nature of the solvent and the method of extraction.^{6–8}

This work is devoted to the extraction of fullerenes from carbon soot obtained in the setup described in Ref. 5. Data on the extraction of fullerenes from soot with various organic solvents were given in many works devoted to extraction of fullerenes.^{6–8} However, it remained unclear how the nature of an organic solvent and the number of cycles of extraction in a Soxhlet apparatus affect the yield and composition of an extract from the soot obtained, which is distinguished by a considerable content of C₆₀ and C₇₀ fullerenes.⁵ It is noteworthy that the choice of conditions of extraction of soots is determined both by their composition, which depends on particular conditions of their preparation, and by peculiarities of the setup design for evaporating graphite in an electric arc.

The extraction of soot samples with various solvents has been studied at room temperature. The subsequent extraction of soot with different solvents according to the toluene (8 cycles) — trichlorobenzene (1 cycle) — nitrobenzene (1 cycle) scheme has also been studied.

Experimental

Fullerenes were extracted with organic solvents by the following procedure. A sample of soot (1 g) in 100 mL of a solvent was stirred for 10 h at ~20 °C and then stored for 12 h. The next day the solution of fullerenes was filtered off, and the solvent was distilled off on a rotor evaporator. The residue obtained was evacuated for 1 h at 90 °C and weighted.

Fullerenes were extracted according to the toluene—trichlorobenzene—nitrobenzene scheme in the following way. The fullerene-containing soot (7.5 g) was placed in a Soxhlet apparatus 1000 mL in volume. Fullerenes were extracted with toluene (1200 mL). After each cycle toluene was distilled off, and the residue was evacuated for 1 h at 90 °C and weighted. After seven extraction cycles with toluene, the sample of soot was treated with 300 mL of trichlorobenzene, stirred with refluxing for 2 h, and then filtered off. The residue obtained after distilling off the trichlorobenzene was washed with ethanol (100 mL) and evacuated at 90 °C for 1 h. Fullerenes remaining in the soot were additionally extracted with 300 mL of nitrobenzene under conditions similar to those of the extraction with trichlorobenzene.

The ratios of fullerenes in extracts were determined spectrophotometrically by a procedure that will be published elsewhere.

Results and Discussion

Such solvents as hexane, benzene, toluene, *etc.*, which are traditionally used for extraction of fullerenes,^{6,9} have been chosen for studying the extraction of soot samples at room temperature (Table 1). Carbon disulfide is excluded from this series due to its toxicity and explosion hazard, although it is known¹⁰ that it dissolves C₆₀ well.

It can be seen from Table 1 that toluene and chlorobenzene make it possible to extract fullerenes efficiently from fullerene-containing soot, and the contents of C₆₀ in toluene and chlorobenzene extracts are approximately equal. Hexane and chloroethylene are distinguished,

Table 1. Influence of the organic solvent on the yield and composition of an extracted fraction of fullerene-containing carbon soot

Solvent	Yield of fraction (%)	C ₆₀ content (%)
Heptane	0.6	63.5
Hexane	0.4	96.0
Trichloroethylene	2.0	85.5
Benzene	3.1	77.5
Toluene*	7.0	76.5
Chlorobenzene	8.3	78.0

* Extraction of this sample of carbon soot with toluene in a Soxhlet apparatus (7 cycles) produces an extracted fraction with a yield of 9.8 % and a C₆₀ content of 77 %.

because they allow one to obtain fractions with a high content of C₆₀. The content of C₆₀ in a hexane fraction reaches 95.6 %; however, a low yield (0.4 %) of hexane-soluble residue makes extraction with hexane relatively inefficient. Not only a low yield (2.0 %) of the soot fraction soluble in trichloroethylene, but also the ability of this solvent to easily form very stable solvates with C₆₀ (Ref. 11) should be counted as disadvantages of trichloroethylene.

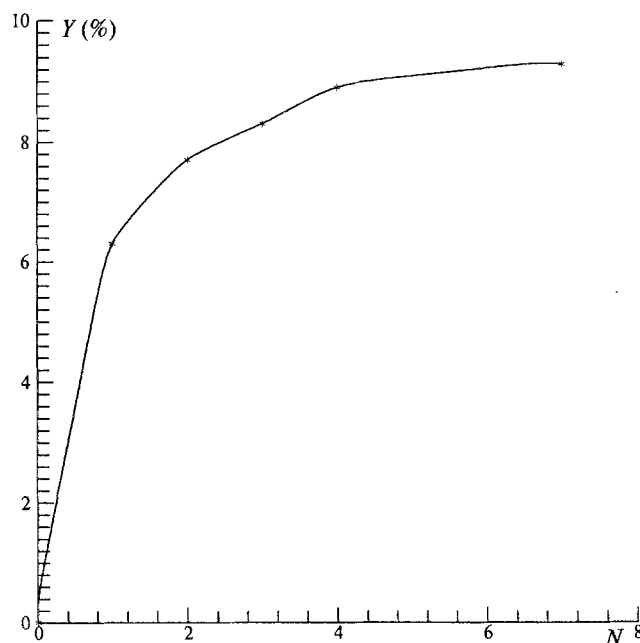
Choosing between toluene and chlorobenzene, we preferred toluene as a less toxic and lower-boiling solvent. Studying conditions of the synthesis of fullerenes in the setup,⁵ the yield and ratio of fullerenes were determined using toluene as extractant.

The dependence of the yield of the toluene extract on the number of cycles in the Soxhlet apparatus is shown in Fig. 1. It can be seen that the greatest portion of fullerenes is extracted from soot with toluene in three to four cycles (the total yield of fullerenes after four cycles is 94 % of the possible yield, Table 2). Since the dependence in Fig. 1 exhibits a tendency for saturation after the seventh cycle, 7 to 8 extraction cycles are needed to determine exactly the yield of fullerenes by toluene extractant, while 3 to 4 cycles are enough for the preparation of the extract. The composition of the fullerene fraction weakly depends on the number of extraction cycles. Only an insignificant decrease in the

Table 2. Yield and composition of the toluene-soluble fraction (7 cycles in the Soxhlet apparatus)*

Number of the cycle	Portion of the fraction extracted in a given cycle (%)	C ₆₀ content (%)	C ₇₀ content (%)
1	67.5	85.38	14.62
2	14.6	85.40	14.60
3	6.2	84.40	15.60
4	6.4	81.13	18.87
5+6+7	5.3	79.37	20.63

* The yield of the fraction after seven cycles is 9.3 %.

**Fig. 1.** Dependence of the yield of the fullerene fraction on the number of cycles in the Soxhlet apparatus for extraction with toluene. *N* is the number of the cycle of registration; *Y* is the yield of the fraction.

content of C₆₀ in the fraction (from 85 % for first three cycles to 79 % for latter three cycles) is observed.

The published data⁷ indicate that additional treatment of soot, which was extracted with toluene, with trichlorobenzene or other high-boiling solvents increases the yield of fullerenes to 40 %. The increase in the yield occurs due to the extraction of higher fullerenes, which are very soluble in these solvents.^{7,12}

We studied toluene, trichlorobenzene, and nitrobenzene extracts of two soot samples obtained under different conditions (Table 3).

According to Table 3, the total yields of fullerenes for different soot samples obtained in the setup⁵ are approximately equal and are 23.8 % for soot I and 26.0 % for soot II. However, the yield of the toluene-soluble fraction of soot I is half that of soot II. It should be mentioned that the treatment of soot I with trichlorobenzene and nitrobenzene after the toluene extraction allows one to additionally extract about 10 % of the fullerenes. Extracts of soot samples differ noticeably in composition. Extracts from soot I contain lower amounts of C₆₀ and higher amounts of higher fullerenes than extracts from soot II. This indicates that the conditions of preparing soots by the electric arc method exert a strong effect on the composition of fullerenes. The total fullerene fractions obtained from the first and second soot samples contain 34 and <20 % of C₇₀, respectively. Thus, to choose optimum conditions for preparing fullerene-containing soots of specified composition, one should carry out both extraction with

Table 3. Yields and compositions of fullerene fractions obtained by the extraction of soot samples according to the scheme: toluene (7 cycles) — trichlorobenzene (1 cycle) — nitrobenzene (1 cycle)

Extract	Soot	Yield (%)	C ₆₀ content (%)
Toluene	I*	13.6	71.0
	I**	24.2	87.3
Trichlorobenzene	I*	7.2	50.0
	I**	1.8	—
Nitrobenzene	I*	3.0	46.1
	I**	—	—

* Soot I was prepared by electric arc evaporation of graphite (OSCh-7-3 trade mark) with alternating current (current on the arc was 130 A, voltage on the arc was 22 V) in a water-cooled reactor 180 mm in diameter with a horizontal arrangement of electrodes (helium pressure was 40 Torr).⁵

** Soot II was obtained in the same reactor, but with a direct-current arc (current on the arc was 60 A, voltage on the arc was 24 V) and a vertical arrangement of electrodes, using the additionally cooled surface of a screwed spiral 80 mm in diameter (helium pressure was 80 Torr).⁵

toluene and extraction with higher-boiling solvents followed by analysis of those extracts.

It should be mentioned in conclusion that the optimization of the soot preparation in the setup⁵ made it possible to find conditions favorable for preparing C₆₀ (soot II with a content of C₆₀ in the toluene-soluble fraction of up to 90 %). Only toluene can be used for extracting fullerenes from this soot.

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