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Extraction of Fullerene Mixture from Fullerene Soot with Organic Solvents

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Abstract—Investigation of extraction of fullerene mixture from the fullerene soot obtained by plasma erosion of graphite rod in helium atmosphere with different solvents such as α-chloronaphthalene, *o*-dichlorobenzene, *o*-xylene, toluene, benzene, carbon tetrachloride, and *n*-hexane at 25°C was carried out. Completeness and effectiveness of extraction as well as relative content of light (C_{60}, C_{70}) and heavy (C_{76}, C_{78}, C_{84}) fullerenes in the extract were evaluated.

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As known, the process of obtaining individual fullerenes is sufficiently complex and includes many stages (see, for example, [1–4]). It consists in several consecutive steps including obtaining the fullerene-containing soot, the isolation of fullerene mixture and separation and purification of individual light (C_{60}, C_{70}) and heavy (C_{76}, C_{78}, C_{84}) fullerenes. Sometimes these stages should be completed with additional ones improving the productivity or the purity of the obtained fullerene products. These stages include recrystallization of fullerene mixture for the separation of the fractions enriched with different individual fullerenes, vacuum Soxhlet extraction of fullerene mixtures from solid phases such as adsorbents, fullerene black, etc. with the purpose of more complete isolation of fullerenes from the waste products of fullerene processes, and so on.

In this work we investigated the process of isolation of fullerene-containing mixture by means of extraction. Fullerenes in contrast to the other polymorphic modifications of carbon such as diamond, graphite, carbine, soot, carbon nanotubes, nanobarrels, and nanobulbs are comparatively well soluble in some organic solvents [5, 6] to form stable real solutions. It makes possible to separate more or less completely the soluble fullerenes from the insoluble carbon components of fullerene soot.

In this work the dependence of completeness of the extraction and fractional composition of the extracted fullerene mixture on the type of solvent (α-chloronaphthalene, *o*-dichlorobenzene, *o*-xylene, toluene, benzene, carbon tetrachloride, and *n*-hexane) was studied. In the case of chloronaphthalene dependence of the above-mentioned characteristics of extraction on temperature was also studied.

In the course of extraction of fullerenes their content in extract was evaluated by three independent methods including a spectrophotometric procedure, a highly effective liquid chromatography, and a direct gravimetry. Results of spectrophotometric evaluation of concentration of fullerenes in extract are presented in Table 1 and in Fig. 1a. The content of heavy fullerenes C_{76}–C_{90} was not taken into account. In Table 2 and in Fig. 1b the results of chromatographic evaluation of the content of fullerenes in extract are compiled. In this case the content of heavy fullerenes was taken into account. In Table 3 the results of direct gravimetric evaluation of fullerene content are presented.

It follows from Fig. 1 and Tables 1–3 that the extraction data obtained by spectrophotometric, chromatographic, and direct gravimetric methods agree with one another despite the first of them does not take into account the content of heavy fullerenes C_{76}, C_{78},

Table 1. Total amount of fullerenes extracted from 300 mg of soot with 30 ml of solvent at 25°C evaluated by spectrophotometric method. Heavy fullerenes are not taken into account

Solvent	Mass of fullerenes $C_{60} + C_{70}$, mg	Content of fullerenes $C_{60} + C_{70}$ in the soot, wt %	Content of fullerene C_{60} in the sum ($C_{60} + C_{70}$), rel. wt %
α-Chloronaphthalene	42	14.0	64
o-Dichlorobenzene	25	8.5	75
o-Xylene	23	7.8	75
Toluene	15	5.0	75
Benzene	16	5.3	71
Tetrachloromethane	14	4.6	76
n-Hexane	1.6	0.53	91

Table 2. Total mass of fullerenes extracted with different solvents (300 mg of fullerene soot, 30 ml of solvent, 25°C) according to HTLC data with accounting for heavy fullerenes[a]

Solvent	Total mass of fullerenes, mg	Content of fullerenes in the soot (summary), wt %	Content of fullerenes C_i in the total mass of fullerenes (relative wt %)					
			C_{60}	C_{70}	C_{76}	C_{78}	C_{84}	$C_{76} + C_{78} + C_{84} + C_{90} + \ldots$
α-Chloronaphthalene	44	14.7	76	24	–	–	–	–
o-Dichlorobenzene	27	9.0	74	24	0.83	0.28	0.59	1.9
o-Xylene	24	8.0	76	22	0.65	0.20	0.52	1.5
Toluene	18	6.0	75	24	0.38	0.14	0.39	1.0
Benzene	16	5.3	78	21	0.34	0.11	0.37	0.9
Tetrachloromethane	6.9	2.3	73	25	1.1	0.44	1.1	2.6
n-Hexane	1.4	0.47	90	10	0.00	0.00	0.00	0.0

[a] Semiqualitative evaluation

and C_{84} in the sample, and that spectrophotometric evaluation is carried out at the analytical wavelength 335.7 nm and 472.0 nm, while the detecting in the course of HPLC process took place at 254.0 nm. The gravimetric detection is the only direct one, and hence it seems to be more reliable.

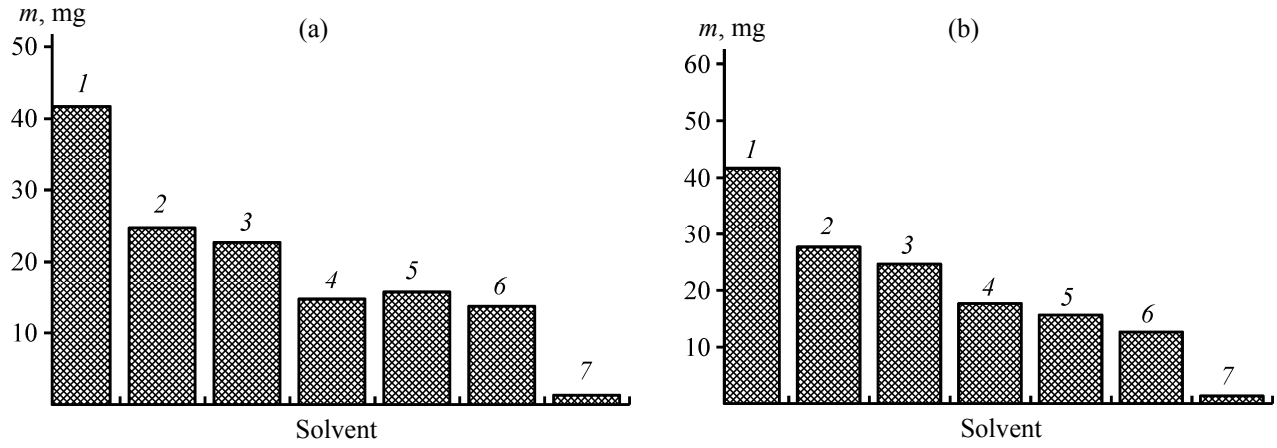

Fig. 1. Amout of light fullerenes $C_{60} + C_{70}$ extracted from 300 mg of fullerene soot at 25°C with different solvents: (a) spectrophotometric measurements, and (b) gravimetric data.

Table 3. Total amount of fullerenes extracted with 30 ml of different solvents from 100 mg of soot at 25°C according to the gravimetric analysis data

Solvent	Total mass of fullerenes, mg	Content of fullerenes in the soot, wt %
α-Chloronaphthalene	44	14.6
o-Dichlorobenzene	28	9.3
o-Xylene	25	8.3
Toluene	18	6.0
Benzene	16	5.3
Tetrachloromethane	13	4.3
n-Hexane	1.7	0.67

In Fig. 2 the content of C_{60} fullerene in the mixtures of fullerenes extracted with different solvents at 25°C according to spectrophotometric and HPLC data are presented. The content of heavy fullerenes in the same mixtures according to HPLC evaluations is reflected in Fig. 3. Data related to α-chloronaphthalene are approximate. The data presented show that fullerene mixtures obtained by the extraction with *o*-dichlorobenzene, *o*-xylene, toluene, benzene, and tetrachloromethane contain approximately the same fraction of the light most widespread C_{60} fullerene, ~74±3 wt %. The mixtures obtained by the extraction with α-chloronaphthalene and *n*-hexane contain the abnormally low and abnormally high fractions of light fullerene C_{60}, 64±1 and 90±1 wt % respectively.

From the data presented in Fig. 3 and Table 2 it follows that relative content of heavy fullerenes C_{76}, C_{78}, and C_{84} and of their sum decreases in the series of solvents including α-chloronaphthalene > tetrachloromethane > *o*-dichlorobenzene > *o*-xylene > toluene > benzene > *n*-hexane. At the same time the content of all heavy fullerenes evaluated by the HPLC analysis in the above presented series of extraction agents alters analogously. Note that the extract obtained by α-chloronaphthalene contains very high part of heavy fullerenes, while in the case of *n*-hexane, the weakest agent, the heavy fullerenes are almost absent (up to the sensitivity of HPLC analysis).

Table 4 compiles the data of mass-spectrometry on the composition of the fullerene mixture obtained by extraction with α-chloronaphthalene.

We have found that the mass of fullerenes extracted with the aliquots of solvents increases with the increase in solubility of light fullerenes (C_{60} and C_{70} separately) at 25°C. This may be due to the fact that both the solubility of fullerenes in solvents and their extraction from the solid phase are determined mainly by the difference in chemical potentials of fullerene components in the solid phase and the solution. In its turn this difference presuming that the liquid solvent is ideal (or more correctly "pseudoideal" [14] when the

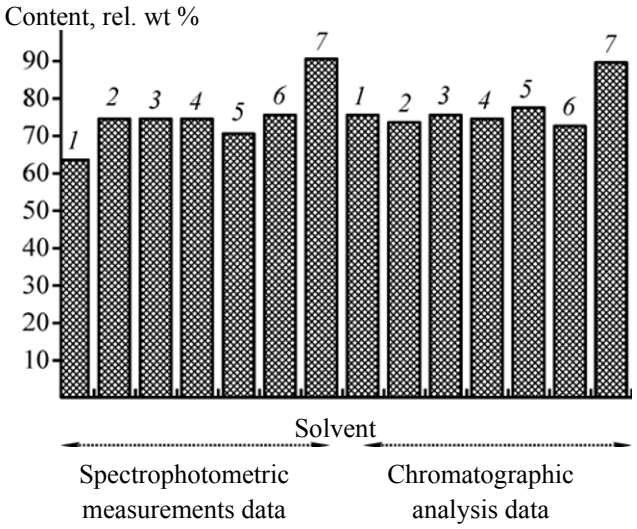

Fig. 2. Content of C_{60} fullerene in the mixture of fullerenes extracted with different solvents ar 25°C according to spectrophometric and HPLC data.

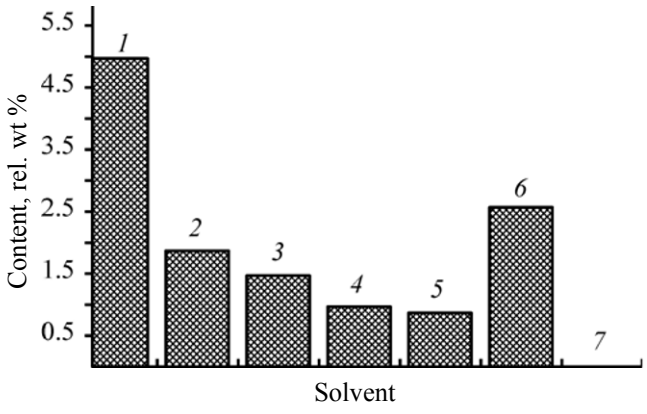

Fig. 3. Content of heavy fullerenes $C_{n>70}$ in the mixtures of fullerenes extracted with different solvents at 25°C according to HPLC data (in the case of α-chloronaphthalene evaluation is approximate).

independence of the activity coefficient on the composition of phase is observed) is proportional just to the logarithm of concentration of fullerene components in liquid solution. But this explanation is yet one-sides because of the following reasoning.

Firstly, the classic equilibrium between the "free" fullerenes in solids and the fullerenes in liquid phase (as it takes place in the studies of phase diagrams of solubility) in our case is overlapped with the additional sorption equilibrium between the fullerenes adsorbed on the fullerene soot and the fullerenes in liquid phase. It must be realized that the complex polyphase adsorbent like the fullerene soot contains adsorption centers with different activity, geometry, etc. That is why the existing quasiequilibrium between the solid and liquid in our case is much more complex than the model we considered.

Secondly, although in the case of α-chloronaphthalene, *o*-dichlorobenzene, *o*-xylene, toluene, and benzene the amount of solvent is sufficient for the formation of unsaturated solutions of fullerene mixture at 25°C, in the case of tetrachloromethane and *n*-hexane in the course of liquid extraction the saturated solutions or quite close to them are formed. Due to that the competition between the adsorption/desorption of fullerenes from the soot and the dissolution/crystallization of fullerenes from liquid solution takes place.

The contribution of these processes for various fullerenes (C_{60}, C_{70}, C_{76}, C_{84}, C_{90} ..) will be evidently different.

Note also that according to mass spectrometry data (see Table 4) in the course of treating the fullerene soot with α-chloronaphtalene quite exotic forms of fullerenes and their derivatives are extracted. In the course of extraction with weaker solvents these forms were not found.

In Fig. 5 and Table 5 the results of extraction of fullerene soot with α-chloronaphthalene in the temperature range 20–80°C are presented. The amount of the extracted fullerenes was evaluated by the direct gravimetry. These data show that the amount of fullerenes extracted increases monotonously with temperature, but above 40°C growth of the amount of substance extracted becomes slower. Mass spectrometric analysis of extracts show that fractional composition of fullerenes extracted is practically independent of temperature.

The facts presented may be commented quailtatively as follows. According to [8] the solubility of the standard fullerene mixture in α-chloronaphthalene depends on temperature quite non-monotonously. That is why the temperature dependence of the extraction completeness cannot be explained only by this factor. On the other hand, it is clear that physical desorption of fullerenes from the surface of fullerene soot is facilitated by the growth in temperature thus increasing the extraction completeness. And finally it is possible that the chemical sorption of fullerenes on the soot increasing with temperature does not affect significantly the adsorption/desorption of fullerenes.

Table 4. Chromatomass spectral data on the composition of extract obtained by the extraction of 300 mg of fullerene soot with 30 ml of α-chloronaphthalene at 25°C. Reflexes are listed according to increase in the retention times of substances

Chromatomass spectral reflex, *m*/*z*	Form of fullerene or its derivative	Relative mass spectral square of the peak
752	$C_{60}O_2$	182
736	$C_{60}O$	1905
720	C_{60}	6023
856	$C_{70}O_{1–2}$	60
912, 936	$C_{76} + C_{78}$	683
984, 1008	$C_{82} + C_{848}$	282
1057, 1081[a]	$C_{88} + C_{90}$	(1322)[a]
1457[b]	$C_{120}O$	–
1488	C_{124}	–

[a] Heavy fullerenes $C_{88} + C_{90}$ are bound with light fullerene C_{60} probably with the sufficiently weak van der Waals forces. The forms determined are probably protonated. [b] $C_{120}O$ form is probably protonated.

The process of extraction of fullerenes includes the stages of the proper dissolution of fullerenes and the filtration, but it is complicated by some circumstances.

Firstly, not all the fullerenes equally well dissolve in organic solvents. The lightest fullerene C_{60} dissolves most eagerly, dissolution of the second light fullerene C_{70} is not so effective, and heavy fullerenes C_{76}, C_{78}, C_{84}, ets. dissolve poorly. Preliminary experiments showed that first portions of fullerenes at the content ~10 wt % of fullerenes in the soot dissolve rather quickly. Dissolution of the subsequent portions at the content of fullerenes 1±0.1 wt % proceeds noticeably slower, and final portions at the content of fullerenes <0.1 wt % are very poorly soluble. Such soot called

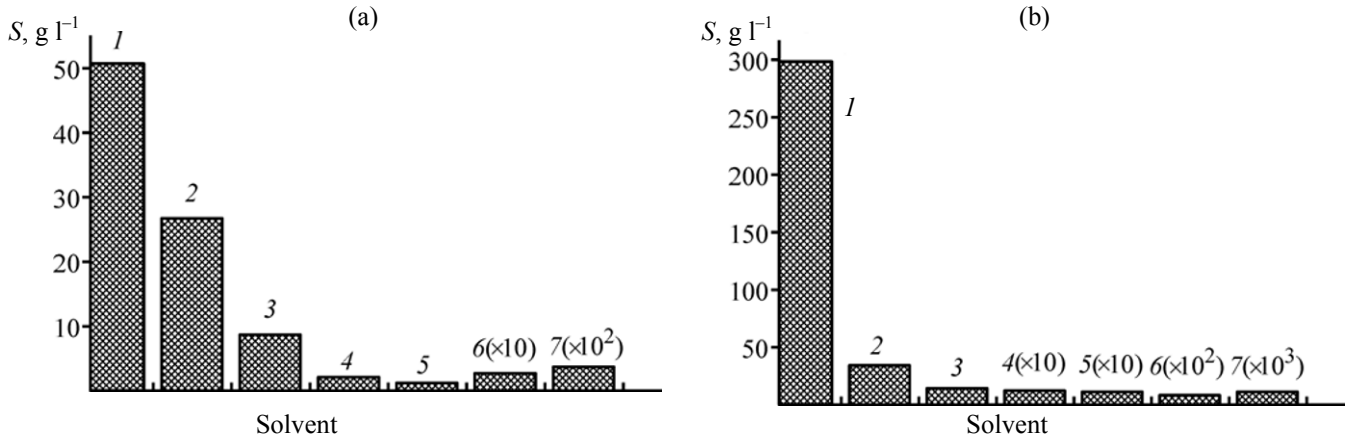

Fig. 4. Solubility of light fullerenes (a) C_{60} and (b) C_{70} in the set of organic solvents at 25°C according to [5].

also the fullerene black contains mainly C_{70} and heavier fullerenes.

Dissolved fullerene molecules can be adsorbed again by the surface of the fullerene soot particles. At the same time the preferred dissolution of one type of fullerenes may be accompanied by the preferred adsorption of another one. This means that in the course of extraction not a simple dissolution equilibrium between the fullerenes in the solid phase and fullerenes in solution takes place, but more complex adsorption-crystallization equilibrium.

Insoluble carbon phases are very finely dispersed, and their separation from the solution obtained is complicated. Typical photographs of the fullerene soot prepared by the ZAO "Innovation of Leningrad Institutes and Plants" at the multiplication 640 were obtained by suspending the portion of soot in the inert solvent (ethyl acetate) at the ratio ~1 mg of soot in 1 ml of solvent, stirring it on the ultrasonic stirrer with the subsequent evaporation of solvent on the glass surface. These photographs show that average linear size of the fullerene soot particles δ is 3±1 μm.

Table 5. Total mass of fullerenes extracted with α-chloronaphthalene according to direct gravimetric analysis data. Extraction of 300 mg of fullerene soot with 30 ml of solvent at 20–80°C

Temperature, °C	Mass of fullerenes, mg	Part of fullerenes in soot, wt %
20	42	14.0
25	44	14.6
40	57	19.0
60	60	20.0
80	66	22.0

The analysis of the dependence of extraction on the type of solvent shows the following picture. The solubility of fullerenes in the set of organic solvents we used forms a series α-chloronaphthalene > *o*-dichlorobenzene > *o*-xylene > toluene > benzene > tetrachloromethane > *n*-hexane. In Fig.4 the solubility of light fullerenes C_{60} and C_{70} in this series of solvents at 25°C is presented. It is based on the data [5] with the addition of the data [8] on the solubility of the fullerene C_{70} in α-chloronaphthalene. As it was shown above the effectiveness of the extraction also decreases monotonously in the series α-chloronaphthalene > *o*-dichlorobenzene > *o*-xylene > toluene > benzene > tetrachloromethane > *n*-hexane. α-Chloronaphthalene, the strongest solvent, exhibits a very high extraction efficiency. Here and below the strength of solvent is determined as the capability of forming more concentrated solutions of fullerenes or their mixtures under the analogous conditions.

The evaluation of effectiveness of extraction agents was carried out at the extraction module value M^{extr} = 10. Under these conditions extraction of fullerenes from the soot is far for complete. For example, in the case of *o*-xylene the extraction is considered complete at the M^{extr} value < 0.5.

In the course of studying the temperature dependence of extraction preliminary experiments have shown that varying temperature in the range 0–60°C causes comparatively weak effect. Nevertheless,

some specific features can be mentioned. For example, in the extraction of fullerenes with *o*-xylene at low temperatures extracted mixture is enriched with C_{60} fullerene, while at high temperatures extraction of C_{70} fullerene is preferred. Further increase in the extraction temperature causes sharp increase in partial pressure of such solvents as α-chloronaphthalene, *o*-dichlorobenzene, *o*-xylene, and toluene. Benzene, tetrachloromethane, and *n*-hexane come to boiling which is technically inconvenient. Besides, at the increase in temperature the processes of chemosorption of fullerenes on the surface of soot, their oxidation with the dissolved oxygen to epoxides $C_{60}O_n$, $C_{70}O_n$, etc., of polymerization and oxo-polymerization of fullerenes leading to $(C_{60})_2$, C_{60}–O–C_{60}, etc. proceed more effectively.

Finally, we can mark that increase in the extraction temperature from ambient to 40–50°C on the whole improves the completeness of extraction with α-chloronaphthalene, the most effective extragent, but it does not alter significantly the composition of the extracted fullerene mixture. The latter effect is probably connected with the weakening of van der Waals interactions (in another words, of physical adsorption) in the fullerene–non-fullerene carbon system at the increase in temperature. At the same time it is evident, that the chemical sorption playing more and more significant role at the temperature growth still does not exhibit the determining effect on the summary extraction process.

Hence, we have shown that the extraction effecttiveness decreases monotonously in the series α-chloronaphthalene > *o*-dichlorobenzene > *o*-xylene > toluene > benzene > tetrachloromethane > *n*-hexane. Only one solvent, α-chloronaphthalene, exhibits extremely high extracting ability in relation to all fullerenes, and especially to the heavy ones. It is established that relative content of heavy fullerenes (C_{76}, C_{78}, C_{84}) and of their sum in the extracted fullerene mixture decreases in the series α-chloronaphthalene > tetrachloromethane > *o*-dichlorobenzene > *o*-xylene > toluene > benzene > *n*-hexane. Among the additional peculiarities of extraction note the abnormally low content of light fullerene C60 (64 wt %) in the case of α-chloronaphthalene, the strongest solvent, and practical absence of heavy fullerenes (up to the sensitivity of HPLC analysis) in the case of *n*-hexane, the undoubtedly weakest solvent. More or less correspondence between the extraction effectiveness and solubility of light fullerenes C_{60} and C_{70} separately at 25°C was demonstrated.

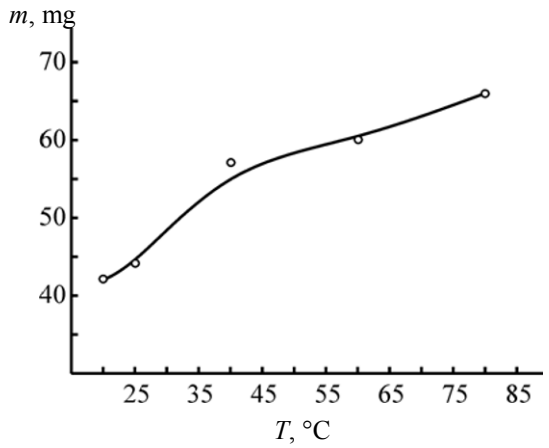

Fig. 5. Amount of fullerenes extracted from 300 mg of fullerene soot with α-chloronaphthalene at 20–80°C depending on temperature according to the gravimetric data.

EXPERIMENTAL

Spectrophotometric measurements were carried out on the Specord M-40 spectrophotometer. Liquid chromatography was carried out on a Lumachrom (Lumex, St. Petersburg) device using the Cosmosil Buckyrep Guard Column (4.6×50 mm).

Chromatomass spectral evaluations were carried out on an Agilent Triple Quard LC/Ms. Microphotographs of the fullerene soot preparation were were taken on a Levenhuk 40L optical microscope.

Fullerene soot was prepared by plasma erosion of graphite rods under helium in ZAO ILIP according to technologies [9–10]. It is a modificartion of the well known Krechmer procedure [11].

Extraction experiments were carried out as follows. The fullerene soot was undersized on the sieve with the pore size δ 40 μm, and the samples with the mass m ~300±1 mg were taken. These samples were treated with V_s = 30±0.1 ml of solvent. The mixtures obtained were shaken in the airtight flask for 60±2 min on a mechanical shaker with the rotation frequency 100 min^{-1} at 25±0.5°C. After that the samples were two times filtered through a paper filter of the "blue band" grade and analyzed spectrophotometrically or by the HPLC method.

Spectrophotometrical method of evaluation of the concentration of light fullerenes C_{60} and C_{70} is thoroughly described in [12]. Measurements were carried out at λ 336.7 and 472.0 nm. The wavelength

fixation accuracy Δλ ±0.5 nm, photometrical accuracy ΔD ±0.005 relative units at the cell thickness l 1 cm.

All measurements were carried out against the pure solvent. For the calculations of concentrations empirical formula obtained for the mixtures of fullerenes in [12] were used.

$$C(C_{60}) = 13.1[D_{335.7} - 1.81D_{472.0}], \quad (1)$$

$$C(C_{70}) = 42.5[D_{472.0} - 0.0081D_{335.7}], \quad (2)$$

where $C(C_i)$ is the concentration of fullerene C_i in the solution, mg l^{-1}, D_i is optical density of solutions at the wavelength $\lambda = i$ and $l = 1$ cm. The concentration of higher fullerenes C_i ($i > 76$) in the solution in these evaluations is neglected. Total error of the evaluation of concentration of light fullerenes C_i (i = 60, 70) was no more than 5% relative.

Evaluation of concentrations of fullerenes in solutions by HPLC method was carried out according to the procedure [13]. The detection was carried out spectrophotometrically at λ = 254.0 nm for the mixed 3:1 methylene chloride-acetonitrile solutions at the overall concentration of the preliminary diluted fullerene solutions of the units of mg l^{-1}. Relative error of the evaluation of concentration of light fullerenes C_i (i = 50, 70) was no more than 3%. Under these conditions not only light, but also heavy fullerenes were detected.

Total mass of extracted fullerenes was evaluated gravimetrically. Solutions of extracted fullerene mixtures of definite volume (usually 10.00±0.02 ml) were placed in the preliminary weighed bottles and evaporated to dryness at 150±5°C and the residual pressure $p < 0.01$ mm for 2 h. After that the bottles were weighed again, and the difference calculated characterized total content of fullerenes in the soot. From the reported data [5, 6] it is known that under these conditions crystal solvates of fullerenes are destroyed and the solvents are evaporated completely [15].

For the quantitative analysis of the solutions of fullerene mixture in α-chloronaphthalene HPLC was not used because at the detecting wavelength 254 nm the absorption bands of fullerenes and solvent overlap, and the absorption of solvent is many times stronger than the absorption of evaluated components.

For the semi-quantitative evaluation of concentrations of fullerenes in α-chloronaphthalene solutions we have used chromatomass spectrometry method.

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REFERENCES

1. Williams, H.A., *The Most Beautiful Molecule. The Discovery of the Buckyball*, John Wiley and Sons, 1997.
2. *Fullerenes*, Sidorov, L.N., Ed., Moscow: Ekzamen, 2005.
3. Ermilov, N.N., Charykov, N.A., Pavlovets, V.A, and Kuznetsova, E.A., *Zh. Innovatsii*, 2007, vol. 110, no 12, p.79.
4. Charykov, N.A., Zuev, V.V., and Kuznetsova, E.A., *Peterburgskii Zh. Elextroniki*, 2007, vol. 53, no. 4, p. 16.
5. Semenov, K.N., Charykov, N.A., Keskinov, N.A., Piartman, A.K., Blokhin, A.A., and Kopyrin, A.A., *J. Chem. Eng. Data*, 2010. vol. 55, p. 13.
6. Korobov, M.V. and Smith, A.L., *Solubility of Fullerenes*, Kadish, K.M. and Ruoff, R.S., Eds., John Wiley and Sons, 2000, p. 53.
7. Storonkin, A.V., *Termodinamika geterogennykh system* (Thermodynamics of Heterogenic Systems), book 1, pt. 1, 2, 1967, Leningrad: Khimiya.
8. Semenov, K.N. and Charykov, N.A., *J. Chem. Eng. Data*, 2010, vol. 55, p. 2373.
9. Abdugaev, R.M., Alekhin, O.S., Gerasimov, V.I., Losev, G.M., Nekrasov, K.V., Charykov, N.A., Nikonov, Yu.A, and Soroka, A.I., Russian Patent no. 2256608, 2005.
10. Abdugaev, R.M., Alekhin, O.S., Gerasimov, V.I., Losev, G.M., Nekrasov, K.V., Charykov, N.A., Nikonov, Yu.A., Soroka, A.I., and Charykov, N.A., Russian Patent no. 39129, 2004.
11. Kratschmer, W., Lamb, L.D., Fostiropoulos, K., and Huffman, D.R., *Nature*, 1990, vol. 347, p. 354.
12. Ponomarev, A.N., Yudovich, M.E., Nikitin, V.A., Nikitin, D.V., Barchenko, V.T., Charykov, N.A., Sobol, V.N., Strel'nikov, K.B., Myshkov, A.I., and Seregin, V.I., *Opt. Spectr*., 2000, vol. 88, no. 2, p. 195.
13. Begak, O.Yu., *Metodika opredeleniya kontsentratsii fullerenov metodom zhidkostnoi hromatofrafii* (Procedure for Evaluation of Concentration of Fullerenes by Liquid Chromatography), VNIIM im. D.I. Mendeleeva, GOST 8.563-96, attestation MVI no. 242/81-2004.
14. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Leningrad: Khimiya, 1966, vol. 1, p. 617.