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Advancement of the Process for Extraction, Chromatography and Characterization of Fullerenes

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Abstract: In the first phase of this work, the basic C₆₀ and C₇₀ as well as the higher fullerenes, mainly C₇₆ and C₈₄, were Soxhlet extracted with *p*-xylene and *n*-heptane from the samples of carbon soot, produced in electrical arc, yielding 5.9% and 0.7% of the extract, respectively. The remaining, *p*-xylene insoluble soot was then extracted with pyridine, by original advanced method, increasing the entire extract yield for an additional 5.9% to 11.8%. The procedures for increases of the basic and higher fullerenes yields, as well as for additional, selective extraction of the higher fullerenes were found. Chromatographic separation of the basic and the higher C₇₆ and C₈₄ fullerenes from *p*-xylene extract was performed by continual elution, in one phase of the process, under atmospheric pressure, with original, defined, gradient of solvents from 5% toluene in hexane to pure 100% toluene, on active Al₂O₃ column, by a new, improved method. Identifications of the basic and the higher fullerenes in chromatographically purified fractions, as well as in the obtained extracts, were performed using determined techniques of IR and UV/VIS spectroscopy that have not been presented previously for the higher fullerenes.

Keywords: Carbon soot, Basic and higher fullerenes, Soxhlet extractions, Chromatography, IR, UV/VIS

INTRODUCTION

The aim of the first stage of this work was to improve the methods for obtaining of the basic and the higher fullerenes from carbon soot in

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increased yields, using different and new solvents or combination of solvents for their extractions. First, carbon soot was extracted with *p*-xylene. Then the remaining soot, insoluble in *p*-xylene, was extracted with pyridine by the original method, and the difference of fullerenes solubilities in these solvents concluded. For comparison, another soot sample was extracted with *n*-heptane, and the yields of all the obtained extracts determined, which hasn't been described previously.

The aim of the second stage of this work was to advance the method for chromatographic separation of fullerenes from the obtained *p*-xylene soot extract by continual elution, in one phase of the process, under atmospheric pressure, with original combined sistem of solvents, from 5% toluene in hexane, and then gradually increasing concentration of toluene in hexane to pure toluene, on active Al_2O_3 column.

The isolation of the higher fullerenes, after the basic, would be a significant advancement in comparison to previous chromatographic methods, whereby only isolation of the basic fullerenes had been achieved (1–24).

Characterization of the obtained chromatographically purified fullerene fractions and the extracts was performed by IR and UV/VIS methods.

The new improved process for obtaining, in increased yields, separation and spectroscopic characterization of the basic and the higher fullerenes was developed.

The IR spectra of chromatographically purified higher fullerenes C_{76} and C_{84} , recorded by KBr technique, have not been presented. Neither has their UV/VIS spectra recorded from hexane been presented, in the range from 200–900 nm.

It is important to emphasize that UV/VIS absorption of C_{84} in the range from 200–900 nm, especially from 200–400 nm, where fullerenes intensively absorb, has not yet been described under any experimental conditions.

The isolated basic and higher fullerenes are significant for further fundamental research and for their possible applications as new nanomaterials in chemistry, medicine, mechanical engineering and technique due to their important properties such as superconductivity, molecular magnetism, catalytic and biological activity (1–10, 25–30).

EXPERIMENTAL

The basic C_{60} and C_{70} and the higher C_{76} and C_{84} fullerenes were Soxhlet extracted from three samples of collected soot (MER Corporation, Tucson, Ariz., USA). The first soot sample (1.7 g) was extracted with *p*-xylene, the second sample (3.04 g) with *p*-xylene and the third sample

(1.8 g) with *n*-heptane. The dissolved *p*-xylene and *n*-heptane extracts appeared brown-red in color. Extractions were performed to complete disappearance of the solvent color in the Soxhlet extraction thimble. Evaporations of the first *p*-xylene extract with a vacuum evaporator yielded 94.8 mg (5.9%), of the second *p*-xylene extract 181.9 mg (5.9–6%), and of *n*-heptane extract 12.6 mg (0.7%) of brown and black solids.

The remaining part of the first soot sample, insoluble in *p*-xylene, was Soxhlet extracted with pyridine. The dissolved pyridine extract appeared yellow-brown and yielded when evaporated the additional 86.7 mg (5.9%) of brown and black solid, increasing the entire extract yield to 11.8% due to the application of the original method.

Separation of the basic and the higher fullerenes from *p*-xylene soot extract (10.4 mg) was achieved by column chromatography on Al₂O₃ (50.1 g), activated 2 hours at 105°C. The sample was dissolved in toluene (few ml), dispersed onto silica (1 g), which adsorbed the solvent producing gelatinous mass, and finally put onto the top of the alumina column. Separated fullerene fractions were obtained by successive elution with the following: 5% toluene in hexane, 10% toluene in hexane, 20% toluene in hexane, 50% toluene in hexane, 67% toluene in hexane, 84% toluene in hexane and 100% toluene, each 250 ml in volume, at a flow rate of 1.5 ml/min. Solution of the first purified fraction appeared purple and yielded when evaporated yellow-brown and black solid. Solution of the second purified fraction was orange-red and yielded when evaporated reddish-brown and black solid. Solutions of the third and the fourth fraction were orange-yellow; solutions of the fifth, sixth and seventh fraction were yellowish and yielded when evaporated brown solids.

IR spectra of all purified fullerene fractions and *p*-xylene soot extract were measured by a Perkin-Elmer FTIR 1725 X spectrometer on KBr substrates from 4000–400 cm⁻¹.

UV/VIS spectra of all purified fullerene fractions and *p*-xylene soot extract were recorded on GBC Cintra 40 spectrophotometer from 200–900 nm. Solutions of fullerenes in hexane, conc. 10⁻³ to 10⁻⁴ mol/dm⁻³, were used.

RESULTS AND DISCUSSION

The IR spectrum of the first purified fullerene fraction of *p*-xylene extract is presented in Figure 1(a). Characteristic, sharp absorption maxima at 525, 576, 1178 and 1428 cm⁻¹, attributed to the four F_{1u} vibration modes of a C₆₀ molecule with icosahedra symmetry, dominate in the fullerene “fingerprint” region from 400 to 1500 cm⁻¹. Absorption at 735 cm⁻¹, common to C₆₀, remains unassigned at this point as it also appears in IR spectra of other C_x chromatographic fullerene fractions. Features

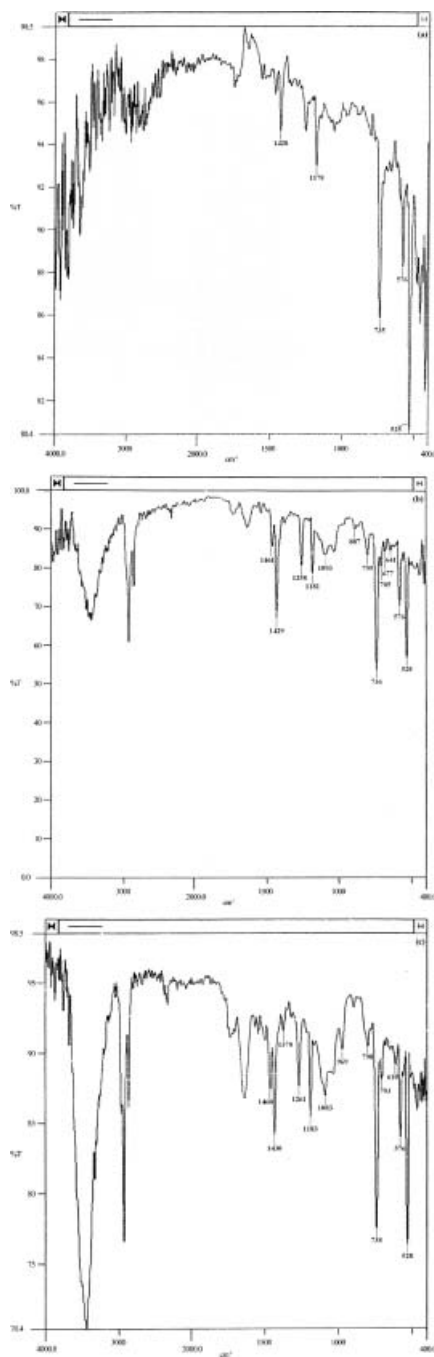


Figure 1. IR spectra of: (a) the first, (b) the second and (c) the third fraction of *p*-xylene extract.

corresponding to other vibration modes of C_{60} appear at 418 and 454 cm^{-1} . Locations and relative intensities of absorption maxima completely correspond to buckminsterfullerene C_{60} , indicating its dominant presence in the first purified fraction (1–12).

The IR spectrum of the second purified fraction is presented in Figure 1(b). Relevant absorption maxima at 528, 576 and 1429 cm^{-1} are moved toward higher frequencies, while their relative intensities have changed in comparison to previous spectrum, which is characteristic for fullerene C_{70} . The weaker bend at 1181 cm^{-1} is also moved toward higher frequency. A series of absorption frequencies unique to C_{70} is registered at 641, 677 and 705 cm^{-1} . Maximum at 736 cm^{-1} , moved toward higher frequency, with a neighbor at 799 cm^{-1} , corresponds to C_{70} . Bends at 1258 and 1461 cm^{-1} are attributed to molecule C_{70} . Absorptions at 407, 441, 887 and 1093 cm^{-1} also correspond to C_{70} . The observed changes of locations and relative intensities of characteristic absorption maxima, as well as the presence of vibration modes unique to C_{70} , indicates the dominant presence of carbon cluster C_{70} in the second fraction (3–12).

The IR spectrum of the third fraction is presented in Figure 1(c). Locations and relative intensities of characteristic absorption maxima at 528, 576 and 1430 cm^{-1} , similarly to previous spectrum, still evidence the presence of fullerene C_{70} in the greatest part in this fraction. Absorption at 703 cm^{-1} , moved toward lower frequency, and sharp bend at 738 cm^{-1} , further moved toward higher frequency, bend at 798 cm^{-1} , with a shoulder at approximately 824 cm^{-1} , as well as weak absorption at 894 cm^{-1} , show the presence of C_{76} besides C_{70} . Despite to previous spectrum, a bit more pronounced absorption bends in the middle part of the relevant region already appear here at 969, 1083 cm^{-1} and a sharp maximum at 1183 cm^{-1} , further moved toward higher frequency due to C_{76} . More intense maxima at 1261 and 1460 cm^{-1} , as well as absorption at 1370 cm^{-1} common to fullerenes spectra, are present. Weak absorption at 1313 cm^{-1} and a shoulder at approximately 1398 cm^{-1} corresponding to C_{76} are observed. Feature at 462 cm^{-1} corresponds both to fullerene C_{70} and C_{76} . Locations and relative intensities of absorption maxima in the whole relevant region indicate the dominant presence of carbon cluster C_{70} still in this fraction (1–9 and the presence of the higher fullerene C_{76} in smaller amount (3–12).

The IR spectrum of the fourth fraction is presented in Figure 2(a). Further changes of relative intensities and locations of characteristic absorption maxima at 527, 577 and 1428 cm^{-1} , here moved toward lower frequencies due to presence of larger amount of C_{76} beside C_{70} , are observed. Bend at 739 cm^{-1} , a neighbor bend at 801 cm^{-1} , with a shoulder at 824 cm^{-1} , moved toward higher frequencies, and absorption at 894 cm^{-1} , corresponding to C_{76} are present. Sharp absorption maxima in the middle relevant part at 968, 1082 cm^{-1} and at 1186 cm^{-1} , further

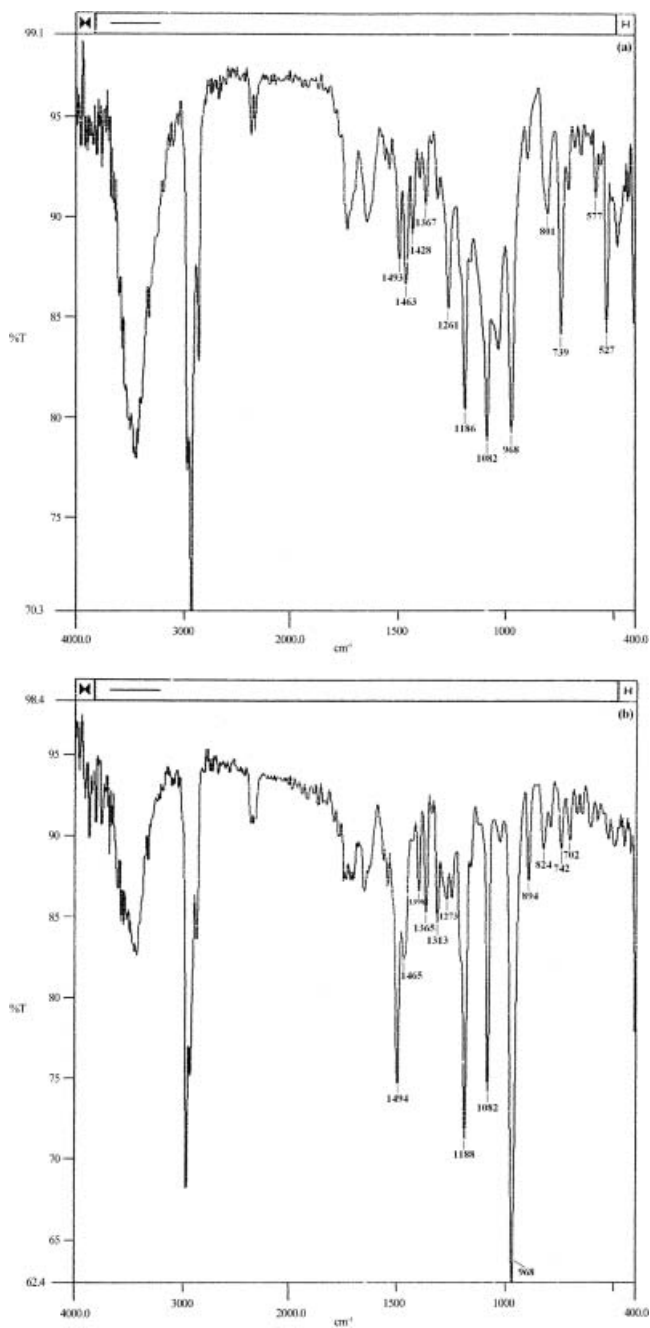


Figure 2. IR spectra of: (a) the fourth and (b) the fifth fraction of *p*-xylene extract.

moved toward higher frequency, are more pronounced and dominant. Maximum at 1261 cm^{-1} and at 1463 cm^{-1} , with a neighbor at 1493 cm^{-1} , moved toward higher frequency, and a bend at 1367 cm^{-1} moved toward lower frequency, also show the increase of amount of the molecule C_{76} . Absorptions at 1313 and 1398 cm^{-1} due to C_{76} appear. Features at 429 and 478 cm^{-1} correspond to C_{76} . Configuration of absorption in this spectrum is evidence of the presence of the higher fullerene C_{76} in larger, significant amounts and the presence of C_{70} still in this fraction in smaller amounts (3–12).

In the IR spectrum of the fifth purified fraction, presented in Figure 2(b), striking changes of relative intensities of the relevant absorption maxima are observed. The main features are three dominant, very intense, sharp, characteristic maxima in the middle relevant region. The first most intense band appears at 968 cm^{-1} , the second at 1082 cm^{-1} , and the third at 1188 cm^{-1} , further moved toward higher frequency, in comparison to previous spectra due to C_{76} . Absorption at 496 cm^{-1} and more intense bend at 742 cm^{-1} , moved on toward higher frequency, with a neighbor at 702 cm^{-1} , moved on toward lower frequency, correspond to C_{76} . Bends at 801 , 824 and 894 cm^{-1} unique to C_{76} are present. Absorptions at 1273 cm^{-1} and at 1465 cm^{-1} , with a neighbor at 1494 cm^{-1} , are also further moved toward higher frequencies, while bend at 1365 cm^{-1} is moved toward lower frequency due to purified molecule C_{76} . Sharp maxima at 1313 and 1398 cm^{-1} unique to C_{76} are registered. Relative intensities and locations of absorption maxima in this significant spectrum indicate the dominant presence of the higher fullerene C_{76} of high purity in the fifth fraction (31–33).

The IR spectrum of the sixth purified fraction is presented in Figure 3(a). In contrast to previous spectrum, absorption in the middle part of the region relevant for identification of fullerenes is not pronounced. Intense vibration bends appear in the two distinct regions: the first from approximately 450 to 850 cm^{-1} and the second from 1050 to 1650 cm^{-1} . In the first part, sharp absorption maxima at 450 and 510 cm^{-1} and four characteristic bends at 711 cm^{-1} , the most intense at 741 cm^{-1} , 780 and 843 cm^{-1} , attributed to the higher fullerene C_{84} , are registered. In the second part, maxima at 1267 and 1462 cm^{-1} are moved toward lower frequencies in comparison to previous spectrum, while bend at 1367 cm^{-1} is moved toward higher frequency, due to C_{84} . Absorption at 1427 cm^{-1} , as well as absorptions at 1516 , 1548 , 1648 cm^{-1} correspond to molecule C_{84} . Complete appearance of the spectrum and locations of absorption maxima indicate the dominant presence of purified higher fullerene C_{84} in the sixth fraction (34, 35).

The IR spectrum of the seventh fraction is presented in Figure 3(b). Similar to previous spectrum, absorption bends appear in the two mentioned regions, significant for C_{84} . Serious of absorptions at 445 , 473 ,

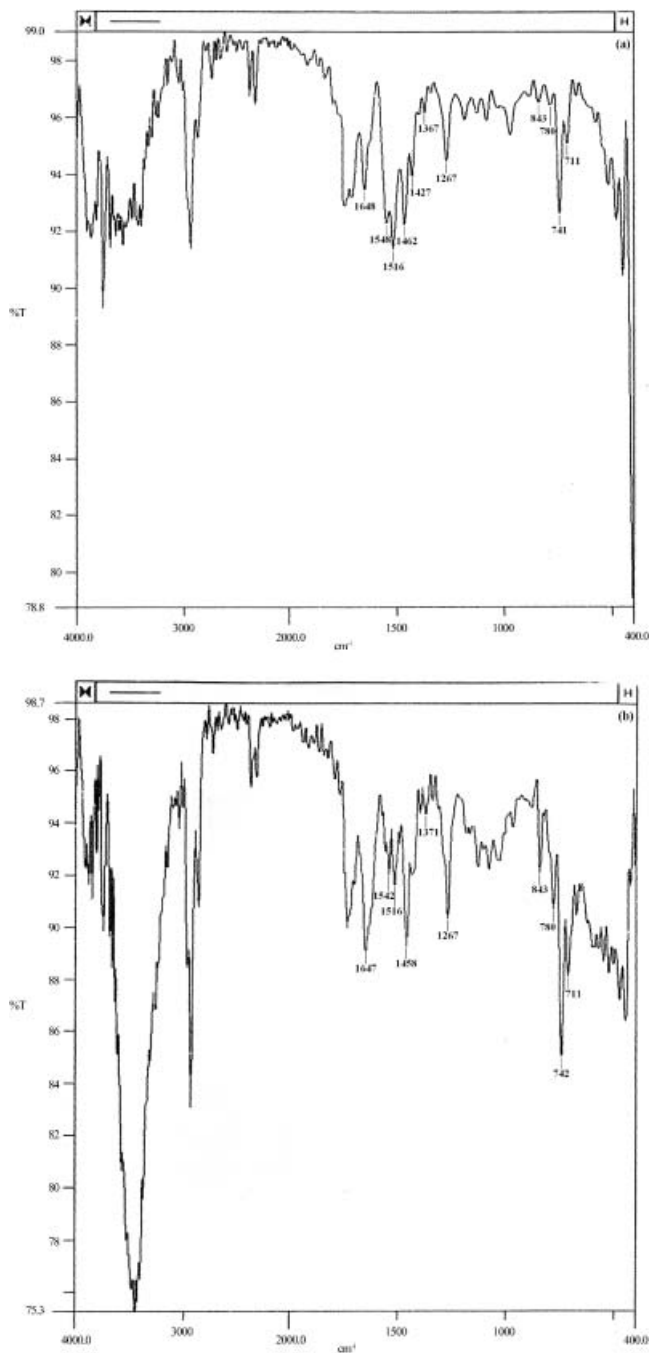


Figure 3. IR spectra of: (a) the sixth and (b) the seventh fraction of *p*-xylene extract.

522, 547 and 672 cm^{-1} , then four relevant, sharp pronounced maxima at 711 cm^{-1} , the most intense at 742 cm^{-1} , at 780 and 843 cm^{-1} , attributed to molecule C_{84} , are present in the first part. Bends at 1267 and 1458 cm^{-1} , further moved toward lower frequency, and at 1371 cm^{-1} , moved on toward higher frequency, with a neighbor at 1339 cm^{-1} , correspond to C_{84} . Absorptions at 1075 and 1127 cm^{-1} , appearing in the second part, as well as at 1516 , 1542 and 1647 cm^{-1} , also correspond to C_{84} . Configuration of absorption in this spectrum evidences the presence of carbon cluster C_{84} of high purity in the seventh fraction as well (34, 35).

The UV/VIS spectrum of the first purified fullerene fraction of *p*-xylene extract is presented in Figure 4(a). Absorption by C_{60} begins in the visible region, at 635 nm, followed by several weak bands of varying width (at *ca.* 621, 598, 591, 568, 542 and 492 nm) and a highly transparent region at 420–440 nm. A weak maximum of the molecule C_{60} appears at 404 nm with a shoulder at 408 nm, followed by distinct shoulders at 396, 391, 377 and 365 nm, appearing on a strong rise toward the first major UV maximum at 328 nm. The ultraviolet region is also dominated by the second, most intense broad bend at 256 nm and the third bend at 210 nm, with a shoulder at 227 nm. Complete absorption corresponds to fullerene C_{60} , evidencing its dominant presence in the first fraction (1–10, 13).

In the UV/VIS spectrum of the second purified fraction presented in Figure 4(b), absorption begins by C_{70} at 650 nm, followed by a series of weak peaks (at *ca.* 637, 624, 610, 600 and 594 nm), superimposed on a gradually rising continuum leading to stronger maxima, attributed to C_{70} , at 550 nm and 470 nm. A broad minimum covers the blue-violet region. Maxima of intermediate strength appear in the near-ultraviolet region at 377 nm and 359 nm on a strong rise toward the first broad UV maximum at 328 nm. The second intense UV bend is present at 256 nm and the third dominant, most intense maximum at 210 nm. Absorption unique to C_{70} in the visible and near-ultraviolet region, and relative intensities of absorption maxima indicate the dominant presence of carbon cluster C_{70} in the second purified fraction (3–10, 13).

The UV/VIS spectrum of the third fraction is presented in Figure 4(c). Bends at 470 and 550 nm in the visible part, as well as absorptions of C_{70} at 378 and 359 nm of slightly decreased intensity, in the near ultraviolet part appear. The first broad UV maximum is located at 328 nm, the second at 256 nm, and the third most intense at 211 nm. Besides, weaker bend at 405 nm, attributed to C_{76} is present in the visible part, while absorption is prolonged to 900 nm. Relative intensities and locations of absorption maxima in this spectrum evidence the dominant presence of fullerene C_{70} still in this fraction, as well as the presence of the higher fullerene C_{76} , in smaller amounts (3–10, 13, 31–33).

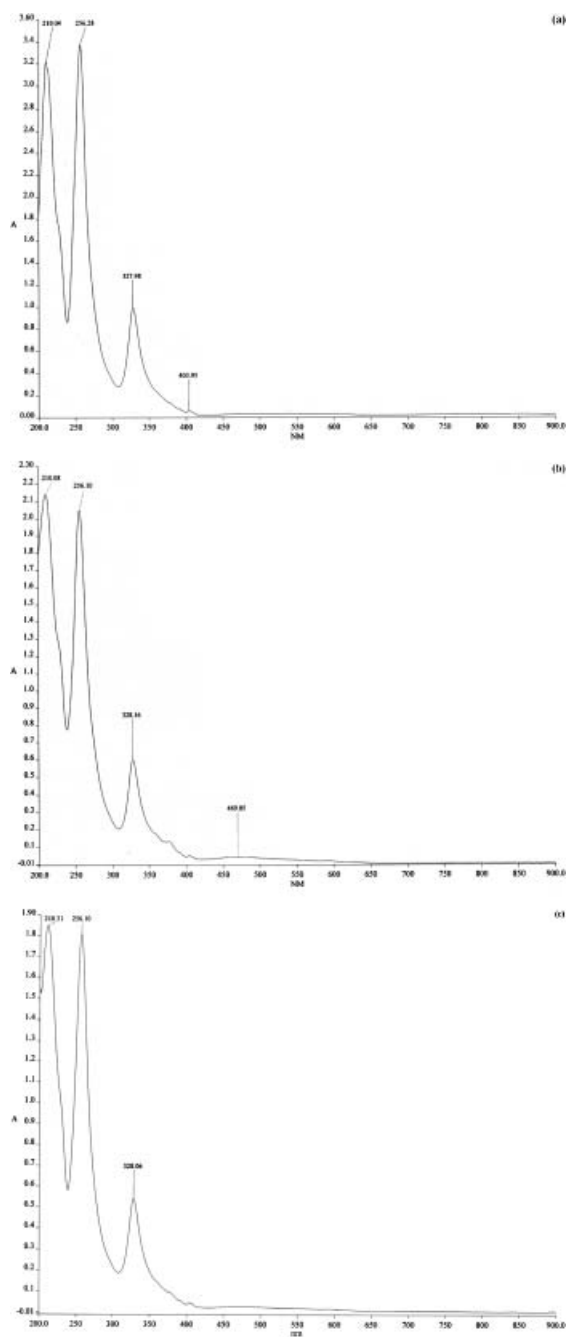


Figure 4. UV/VIS spectra of: (a) the first, (b) the second and (c) the third fraction of *p*-xylene extract.

In the UV/VIS spectrum of the fourth fraction, presented in Figure 5(a), significant changes of relative intensities of characteristic absorption maxima at 328 and 256 nm are registered, while the third most intense with a shoulder at 210 nm is moved to the region below 200 nm. Absorptions at 550, 470, 378 and 359 nm of decreased intensities are observable. A bend at 405 nm and absorption prolonged to 900 nm due to C_{76} appear. Complete absorption in this spectrum indicates the presence of the higher fullerene C_{76} , in a larger amount and of molecule C_{70} , in a smaller amount (3–10, 13, 31–33).

The UV/VIS spectrum of the fifth fraction, presented in Figure 5(b), is different from previous spectra. Further abrupt changes of relative intensities of significant maxima at 257 nm and 327 nm are observed, as well as a band at 405 nm, corresponding to molecule C_{76} . Absorption in the visible part is prolonged to 900 nm. Complete configuration of this spectrum indicates the dominant presence of purified higher fullerene C_{76} in the fifth fraction (31–33).

The UV/VIS spectrum of the sixth purified fraction, presented in Figure 6(a), has shown the new properties in comparison to previous spectra. Characteristic series of absorption maxima, precisely at 252, 261, 272, 287, 304, 319, 334 and 357 nm, attributed to the higher fullerene C_{84} is registered. In the visible part, absorption is prolonged to 900 nm. All absorption bends in this spectrum correspond to carbon cluster C_{84} , as evidence of its dominant presence in the sixth fraction (31).

The UV/VIS spectrum of the seventh purified fraction, presented in Figure 6(b), is similar to the previous spectrum. Series of absorption maxima at 252, 261, 272, 287, 304, 319, 334, and 357 nm, corresponding to C_{84} is present. The bends of carbon cluster C_{84} at 223, 231, 236 and 240 nm are also clearly observed. Complete absorption in the spectrum indicates the dominant presence of the higher fullerene C_{84} in the seventh fraction (31).

Characteristic properties, the unique bends, changes of relative intensities and locations of absorption maxima are observed, showing separation and isolation of the basic and the higher fullerenes. The results of UV/VIS analysis are in agreement with the results of IR analysis. IR and UV/VIS spectra of purified C_{76} or C_{84} fractions, that we obtained in other processes showed similar or identical properties.

CONCLUSION

In the first part of this work, the basic fullerenes C_{60} and C_{70} , and the higher fullerenes, mainly C_{76} and C_{84} , were Soxhlet extracted from carbon soot samples with *p*-xylene and *n*-heptane. The yields of the both obtained *p*-xylene soot extracts were 5.9%, while *n*-heptane extract yield

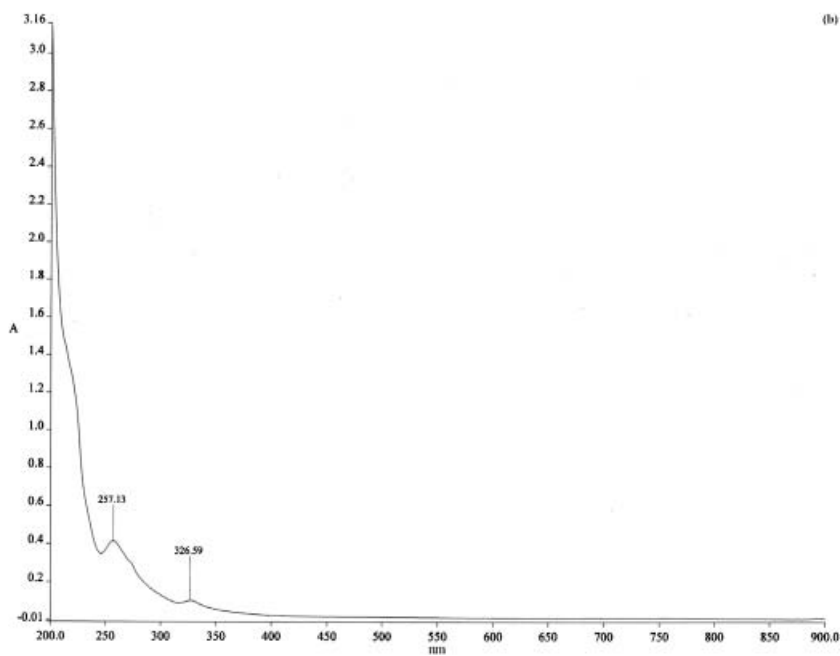
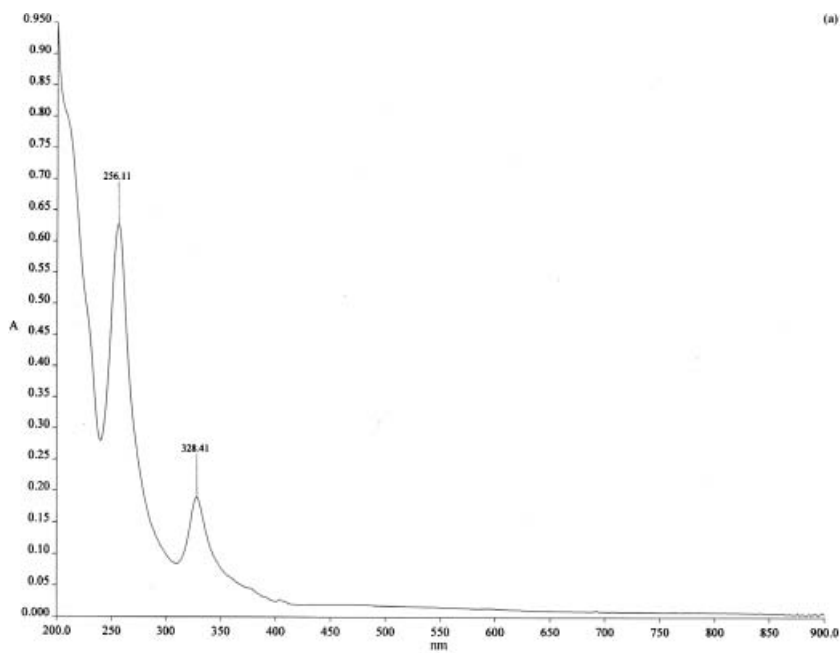


Figure 5. UV/VIS spectra of: (a) the fourth and (b) the fifth fraction of *p*-xylene extract.

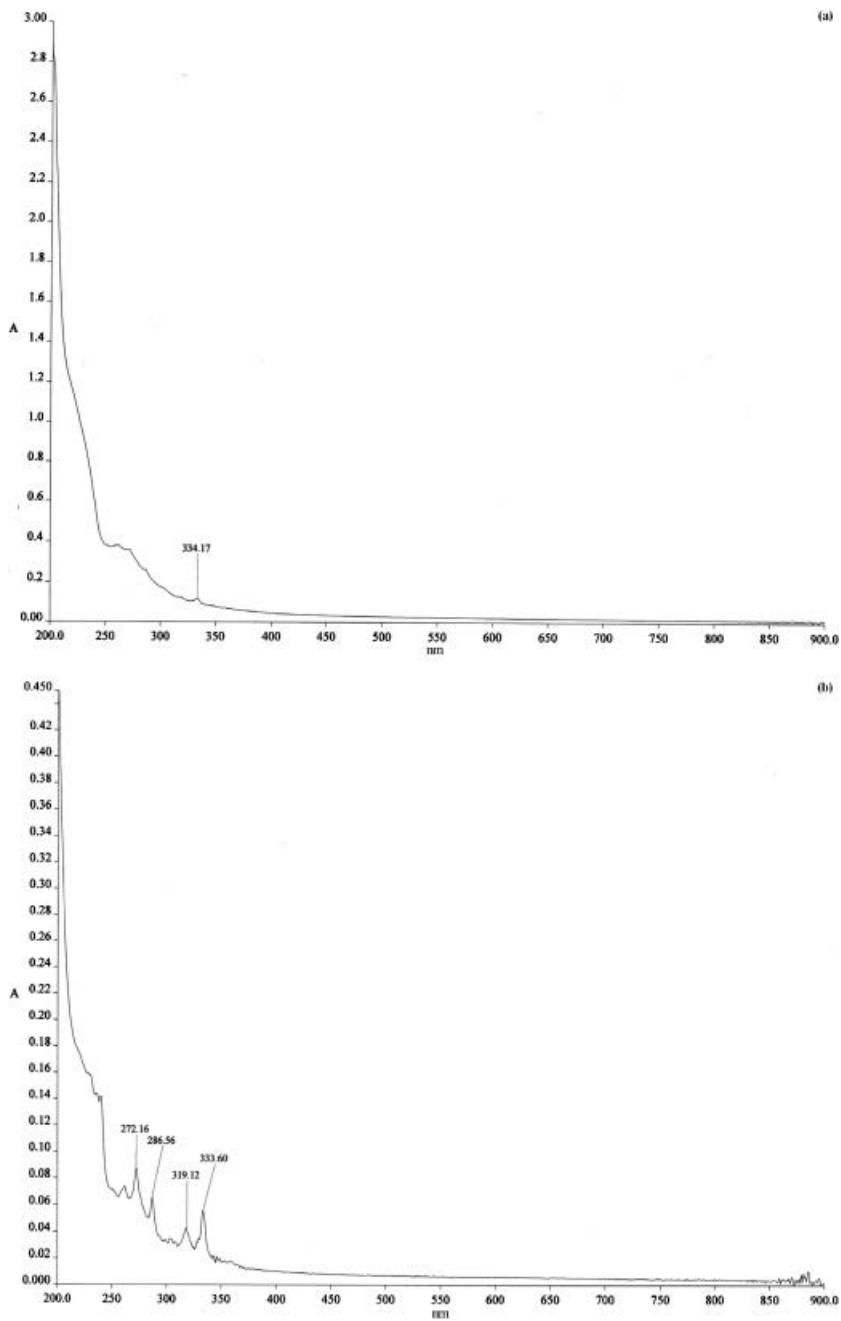


Figure 6. UV/VIS spectra of: (a) the sixth and (b) the seventh fraction of *p*-xylene extract.

was 0.7%. Applying the extraction of the remaining, *p*-xylene insoluble soot with pyridine, the entire extract yield was increased from 5.9% to 11.8% due to the original improved method. Comparing the results obtained with *n*-heptane, previously obtained by Krätschmer et al. (1%) (28), to yields previously obtained with toluene (5.4%) and chlorobenzene (5.8%) (6–8), and using new method with *p*-xylene and pyridine, further and significant increases of fullerenes yields were achieved, as well as the additional, successive extraction of higher fullerenes.

In the second part of the work, *p*-xylene soot extract was separated by the new improved method on the active alumina column by continual elution in one phase of the process, under atmospheric pressure, with original, defined system of solvents from 5% toluene in hexane to pure toluene.

All chromatographically purified fullerene fractions were analyzed by IR and UV/VIS spectroscopy. The dominant presence of buckminsterfullerene C₆₀ was indicated in the first purified fraction, of fullerene C₇₀ in the second, the appearance of both molecules C₇₀ and C₇₆ in the third and the fourth fraction, in different ratios, the presence carbon cluster C₇₆ of high purity in the fifth and of purified higher fullerene C₈₄ in the sixth and the seventh fraction.

Isolation of the higher fullerenes C₇₆ and C₈₄, after the basic C₆₀ and C₇₀, by newly developed chromatographic method represents significant advancement in comparison to previous methods by which only the basic fullerenes were obtained (1–24).

The advantage of this method in comparison to chromatographic methods under pressure (31, 36, 37) is in continual elution in one phase of the process, under atmospheric pressure, and smaller flow of 1.5 ml/min, successively, in increased milligrams yields. The other advantages are the employment of smaller volumes of solvents, smaller masses of stationary phase, finely granulated Al₂O₃, as well as cheaper laboratory equipment.

IR and UV/VIS analysis of *p*-xylene soot extract confirmed the result of its chromatographic separation, indicating that this extract contains in greatest part the basic C₆₀ and C₇₀ fullerenes, as well as significant amount of the higher C₇₆ and C₈₄ fullerenes. Also, IR, UV/VIS, and adequate chromatographic analysis of the additional pyridine extract indicated better solubility of the higher fullerenes, in greatest part C₈₄ and C₇₆ in pyridine then in *p*-xylene.

On the basis of the obtained results, it is concluded that these suitable methods and processes can be used in practice for obtaining the basic and higher fullerenes of high purity in increased yields.

The original spectra in this article will significantly contribute to better introduction of properties and possibilities for identification of this new class of nanomaterials, for the necessity of projections and production of nanocontrol systems.

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