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# Advances in Chromatographic Separation on Al<sub>2</sub>O<sub>3</sub> and Spectroscopic Characterization of the Higher Fullerenes

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*The basic C<sub>60</sub> and C<sub>70</sub>, and the higher fullerenes, mainly C<sub>76</sub> and C<sub>84</sub> were extracted with a series of different and previously unapplied solvents or combinations of solvents, by original advanced procedures, from the samples of carbon soot, produced in electric arc. The solubility of the basic and the higher fullerenes in the applied series of solvents was compared. Chromatographic separations of fullerenes from the obtained extracts were performed by continue elution, in one phase of each process, under atmospheric pressure, with the original, defined gradients of solvents, from pure hexane or 5% toluene in hexane to pure toluene, on active Al<sub>2</sub>O<sub>3</sub> columns, by the new, improved methods. Identifications of fullerenes in all the chromatographically purified fractions and the extracts were performed using determined techniques of IR and UV/VIS spectroscopy that have not been presented previously for the higher fullerenes. The advances in chromatographic purification using alumina, as well as in understanding of the unique and the main optical absorption properties of these molecules are reported.*

**Keywords** Carbon soot, higher fullerenes, solvent extractions, alumina column chromatographies, optical absorption properties

## Introduction

The isolation of fullerene C<sub>60</sub> as the first fullerene fraction was obtained by column chromatography, using Al<sub>2</sub>O<sub>3</sub> as the stationary phase, with either pure hexane or 5% toluene in hexane as eluent (1–6). Successful and advanced separations, as well as characterizations, of the basic fullerenes C<sub>60</sub> and C<sub>70</sub> from the obtained soot extracts were achieved with the different original, defined gradients of solvents, from pure hexane to 20% benzene, toluene, or xylenes in hexane (7–10), respectively, at ambient conditions.

In the previous investigation (11), the purified basic fullerenes were isolated using alumina flash chromatography column without application of pressure in the first stage, while the purified higher fullerenes C<sub>76</sub> and C<sub>84</sub> were obtained in the next stage on the same column under pressure, using hexane-toluene gradient elution, and then by repeated chromatography.

The main aim of this research was to further develop, advance, optimize and at the same time simplify and increase the efficiency of chromatographic methods for obtaining

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of purified basic and higher fullerenes, using  $\text{Al}_2\text{O}_3$  as the stationary phase material. Chromatographic separations of fullerenes from the obtained soot extracts were performed by continue elution, in one phase of each process, with the several different original combined systems of solvents: from pure hexane, or 5% toluene in hexane, and then gradually increasing concentration of toluene in hexane to pure toluene (12–14), including the new process described in this article.

Characterizations of all the purified fullerene fractions and the extracts were performed by determined techniques of IR and UV/VIS spectroscopy that have not been presented previously for the higher fullerenes, in the regions where they intensively absorb.

The obtained results of spectroscopic characterization of chromatographically purified fractions of the higher fullerenes  $\text{C}_{76}$  and  $\text{C}_{84}$  from this research were analyzed and compared among themselves and with the previously obtained theoretical and experimental results, by other techniques (11,15–26).

## Experimental

The basic  $\text{C}_{60}$  and  $\text{C}_{70}$ , and the higher fullerenes, mainly  $\text{C}_{76}$  and  $\text{C}_{84}$ , were Soxhlet extracted with the previously unapplied series of solvents and combinations of solvents from the samples of carbon soot, produced in electric arc (MER Corporation, Tucson, AZ, USA), such as *n*-heptane, toluene, chlorobenzene, *p*-xylene, *o,m,p*-xylenes and pyridine, as well as successively with *p*-xylene and pyridine and with toluene and chlorobenzene. Extractions were performed to complete disappearance of the solvents color in the Soxhlet extraction thimble.

Separations of the basic and the higher fullerenes from the obtained soot extracts were achieved using column chromatographies on  $\text{Al}_2\text{O}_3$  (ca. 50 g per chromatography), activated for 2 hours at  $105^\circ\text{C}$ . The elutions were performed with the several different original, defined systems of solvents: from pure hexane or 5% toluene in hexane and then gradually increasing concentration of toluene in hexane to pure toluene (12–14), including the new, fourth process described in this article, at a flow rate 1.5 ml/min. The employed amounts of solvents per chromatography were from 1.5 to 1.75 l. Before separation, each sample of the extract (ca. 10 mg) was dissolved in hexane and toluene (few ml), dispersed onto silica (1 g), which adsorbed the solvent producing gelatinous mass, and finally put onto top of the new alumina column.

Chromatographic separation of fullerenes from the second additional pyridine extract (10.1 mg), obtained by extraction of *p*-xylene insoluble soot with pyridine, was performed by successive elution with the following: 5% toluene in hexane, 15% toluene in hexane, 25% toluene in hexane, 50% toluene in hexane, 75% toluene in hexane and 100% toluene, each 250 ml in volume. Solutions of all the isolated fractions were yellowish and yielded when evaporated brown solids.

IR spectra of all the chromatographically purified fullerene fractions, as well as of fullerenes soot extracts from this research were measured by a Perkin-Elmer FTIR 725 X spectrometer by KBr disk technique, from 400 to  $4000\text{ cm}^{-1}$ .

UV/VIS spectra of all the purified fullerene fractions and of the extracts were recorded on GBC Cintra 40 spectrophotometer, from 200–900 nm. Solutions of fullerenes in hexane, conc.  $10^{-3}$  to  $10^{-4}\text{ mol/dm}^3$  were used.

UV/VIS spectra of all the purified fullerenes fractions and of the extracts were also recorded on a Perkin-Elmer Lambda 5 spectrophotometer, from 200–900 nm, using both solutions of fullerenes in hexane, conc.  $10^{-3}$  to  $10^{-4}\text{ mol/dm}^3$  and much diluted solutions of fullerenes in hexane, to complete discoloring, for comparison.

In this article, four characteristic processes for chromatographic separation and spectroscopic characterization of fullerenes from carbon soot samples are presented graphically. The obtained masses of the purified fullerene fractions are reported.

Chromatographic separation and spectroscopic characterization of the basic and the higher fullerenes from the obtained first *p*-xylene soot extract (10.4 mg) is presented graphically in Figure 1.

The obtained masses of the isolated fullerene fractions from the first *p*-xylene soot extract were: 1) 2.7 mg, 2) 1.8 mg, 3) 0.9 mg, 4) 0.9 mg, 5) 1.0 mg, 6) 1.8 mg and 7) 1.3 mg.

Chromatographic separation and spectroscopic characterization of the basic and the higher fullerenes from the obtained second *p*-xylene soot extract (10.03 mg) is presented graphically in Figure 2. The first fraction was collected twice (labeled as first and first') due to small differences in the color shade. In the 1' fraction besides the dominant presence of C<sub>60</sub>, the presence of small amount of C<sub>70</sub> was indicated.

The obtained masses of the isolated fullerene fractions from the second *p*-xylene soot extract were: 1) 2.9 mg, 1') 2.1 mg, 2) 1.0 mg, 3) 1.3 mg, 4) 1.7 mg and 5) 1.0 mg.

Chromatographic separation and spectroscopic characterization of fullerenes from the first pyridine extract of the initial soot (10.0 mg) is presented in Figure 3.

The obtained masses of the isolated fullerene fractions from the first pyridine extract of the initial soot were: 1) 2.0 mg, 2) 1.4 mg, 3) 1.3 mg, 4) 0.9 mg, 5) 1.2 mg and 6) 0.9 mg.

Chromatographic separation and spectroscopic characterization of fullerenes from the second, additional pyridine extract (10.1 mg) is presented in Figure 4.

The obtained masses of the isolated fullerene fractions from the second, additional pyridine extract of *p*-xylene insoluble soot were: 1) 1.5 mg, 2) 1.2 mg, 3) 1.3 mg, 4) 0.9 mg, 5) 1.2 mg and 6) 1.1 mg.

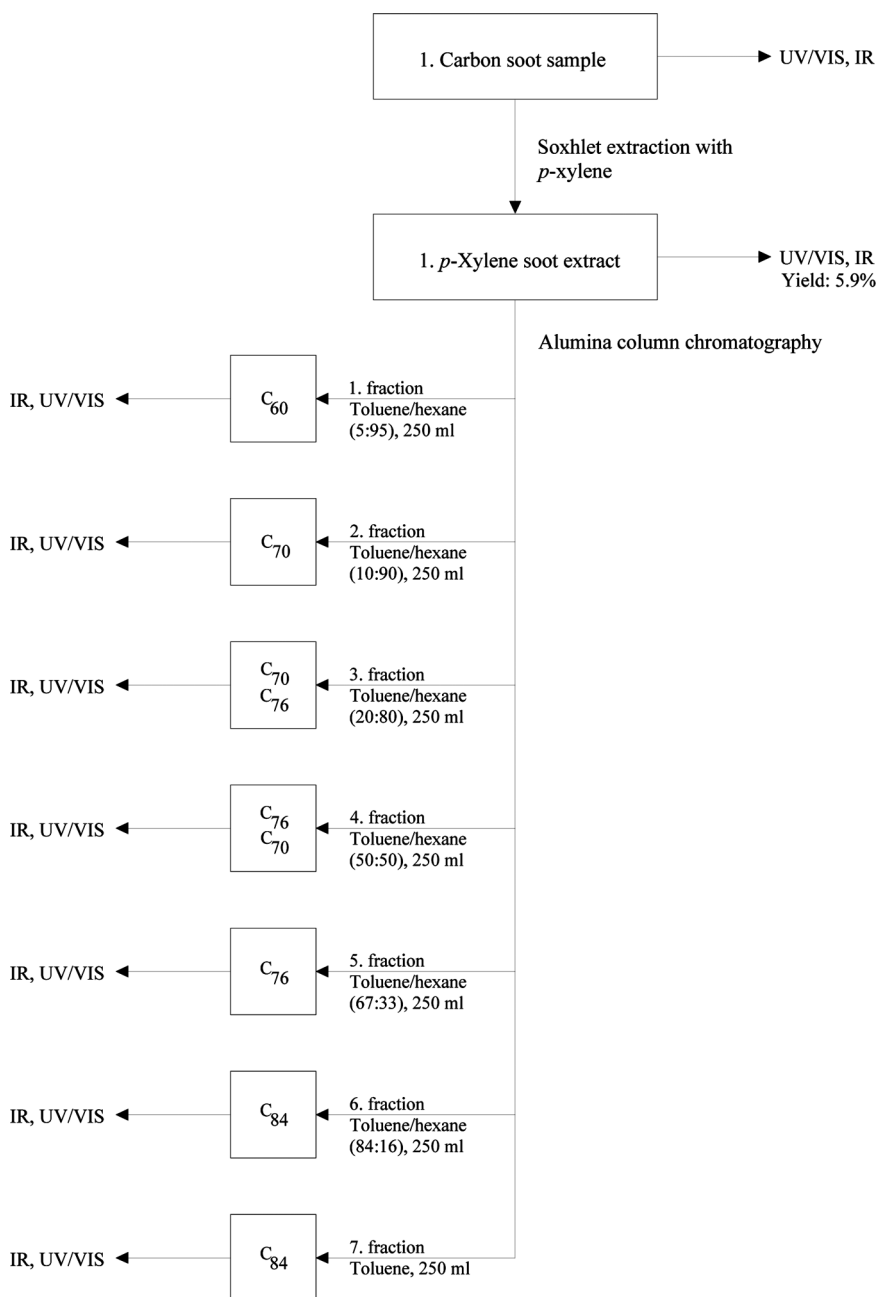
Besides the presented chromatographic methods for efficient separation of the basic and the higher fullerenes at environment conditions, these protocol schemes may be utilized for HPLC with eventual recycle of not purified fractions.

## Results and Discussion

In this article, the differences in the observed spectroscopic details of the isolated higher fullerenes C<sub>76</sub> and C<sub>84</sub> from this research in comparison to previous separation processes are discussed. The achieved advances in their characterization and separation are described, which has not been reported previously. The IR and UV/VIS optical absorption maxima of all the purified C<sub>76</sub> and C<sub>84</sub> samples from the several different separation processes in this research (12–14), including the new process described in this article are in excellent agreement.

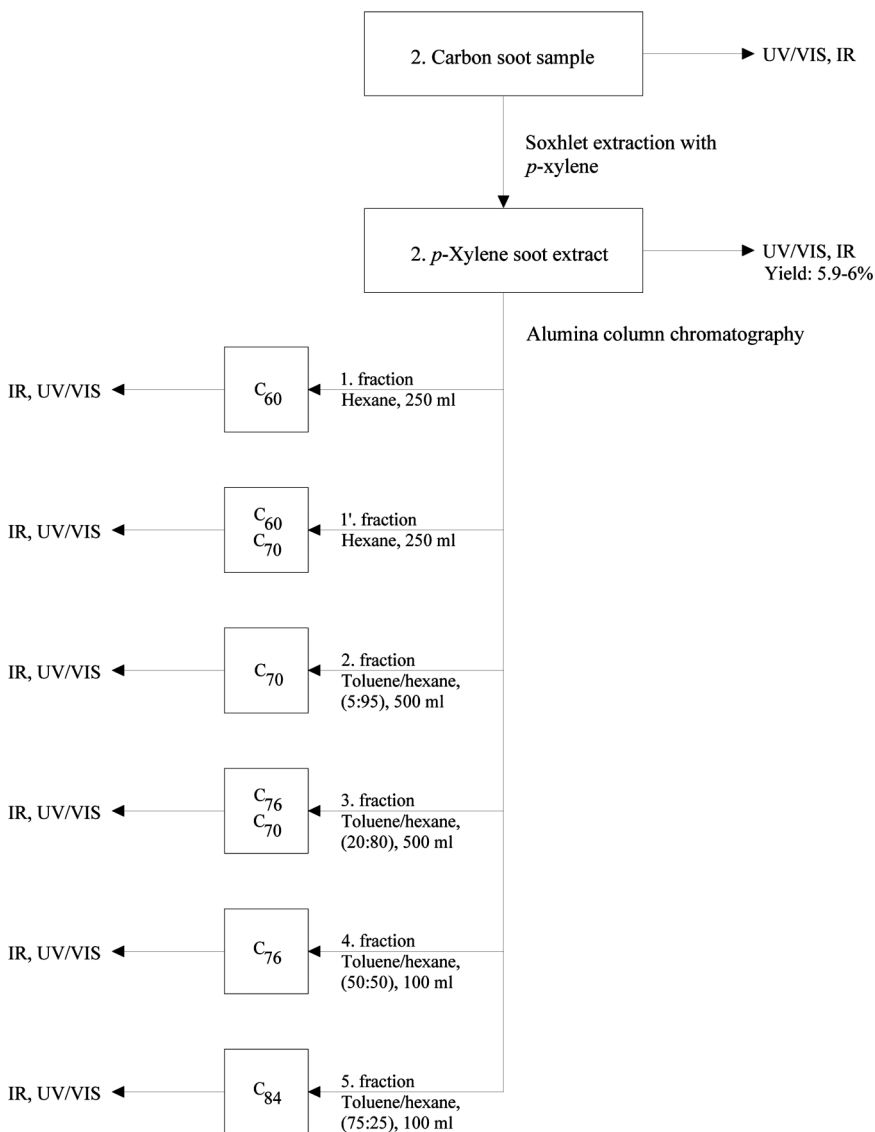
It is important to emphasize that all the experimentally obtained absorption bands of chromatographically purified fractions of the higher fullerene C<sub>76</sub> from the separation processes in this research (12–14), including the new process, are also in agreement with theoretically calculated IR active vibration modes for the only stable C<sub>76</sub> isomer of D<sub>2</sub> symmetry, by Orlandi et al. (from entirely 165 possible modes) (15). This has not been reported previously and represents a significant advancement. The agreement (12–14,15) is better in comparison with previous characterizations of C<sub>76</sub> from other separation processes, by other IR techniques (15–17). It is accurate in the whole region relevant for identification of fullerenes, from 400 to 1650 cm<sup>-1</sup>.

In the previous study some discrepancies between the experimental and theoretical results for C<sub>76</sub> were obtained in the regions around 1000–1050, 1100–1200 and 1500–1600 cm<sup>-1</sup> of 40–60 cm<sup>-1</sup> (15,16). The observed IR features of the higher fullerene



**Figure 1.** The first process for chromatographic separation and spectroscopic characterization of fullerenes from the obtained first *p*-xylene soot extract.

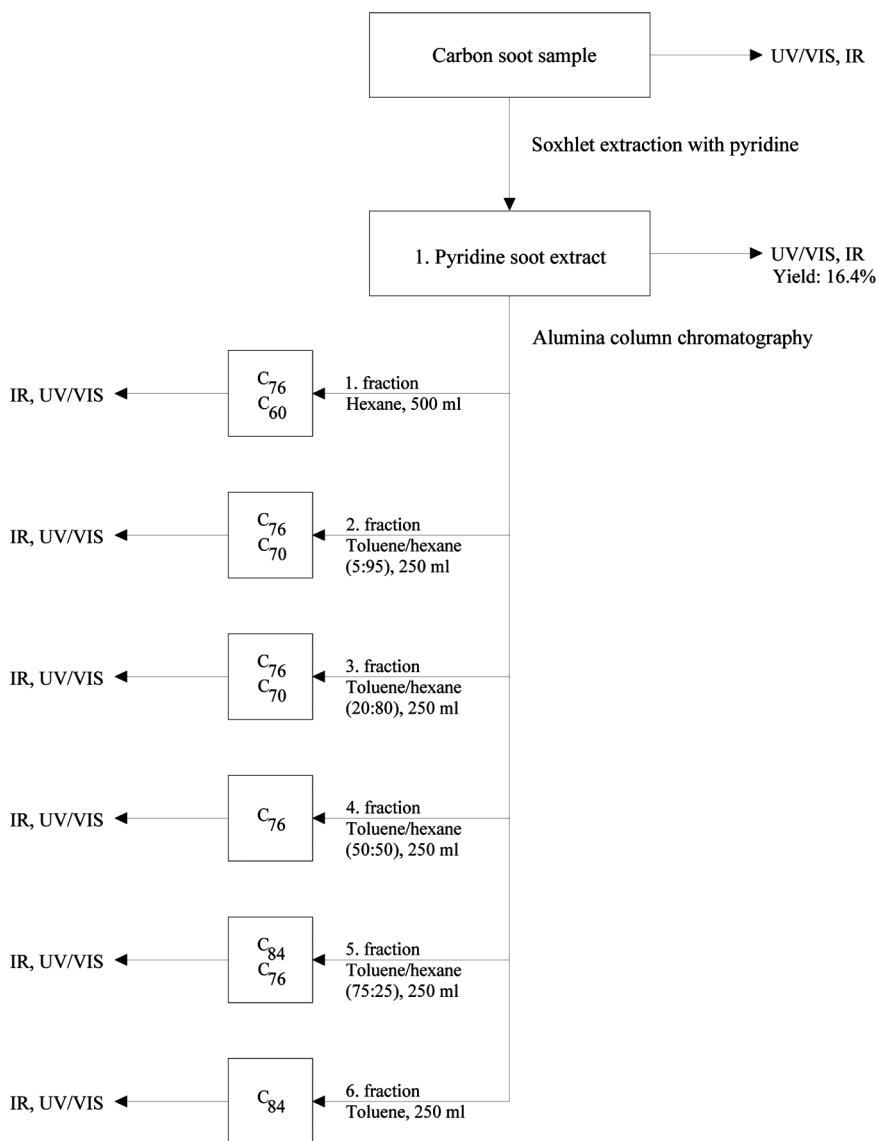
C<sub>76</sub> from another separation process were tentatively rather assigned to a subset of fundamental vibrations, although there was presumption that some of these features may be weaker overtone or combination bands (17), what our results (12–14) also suggest. The IR measurement in this study (17) was not in agreement with the mentioned first published spectrum of C<sub>76</sub> (16), suggesting that the previous measurement was carried out with an



**Figure 2.** The second process for chromatographic separation and spectroscopic characterization of fullerenes from the second *p*-xylene soot extract.

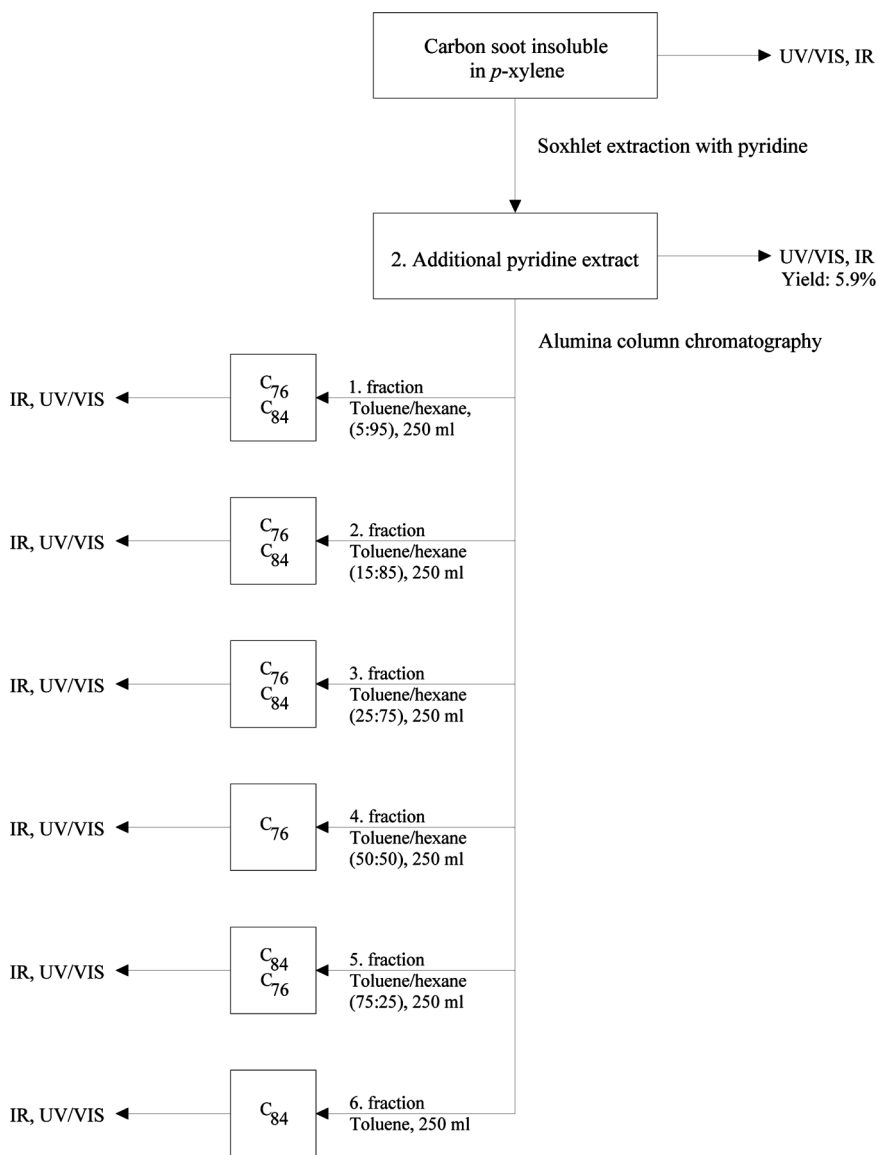
impure sample. In this later study (17) larger number of features was observed and also some discrepancies between experimental results and theoretical calculations (15,17) in the central significant part of the spectrum, around  $1020\text{--}1030\text{ cm}^{-1}$  of up to  $26\text{ cm}^{-1}$ . In several cases, two experimentally obtained features were very close or corresponded to one and the same theoretically calculated  $C_{76}$  vibration mode (15,17).

In our research, pronounced, characteristic absorption maxima unique to the higher fullerene  $C_{76}$  are registered in the significant central part of the spectrum from *ca.*  $800$  to  $1200\text{ cm}^{-1}$ , as well as in the region from *ca.*  $1310$  to  $1400\text{ cm}^{-1}$ , in precise agreement with theoretical calculations, which has not been reported previously, as another important advancement.



**Figure 3.** The third process for chromatographic separation and spectroscopic characterization of fullerenes from the first pyridine extract of the initial soot.

The main advantage of our characterization compared with previous experimental results for  $C_{76}$  is the observation of the main, dominant, sharp, very intense  $C_{76}$  features in all the IR spectra of chromatographically purified fractions of this molecule, in the middle part of the region relevant for identification of fullerenes, at precisely 968, 1082 and 1188  $\text{cm}^{-1}$ . Characteristic, sharp absorption bands unique to the higher fullerene  $C_{76}$  are also registered in this study at 824 and 894  $\text{cm}^{-1}$  in the first relevant part, as well as at 1313 and 1398  $\text{cm}^{-1}$  in the second relevant part of the spectrum. The absorptions at 1494, 1541, 1635 and 1646  $\text{cm}^{-1}$  appear in the region from 1500–1650  $\text{cm}^{-1}$ , which has not been presented. All the other obtained  $C_{76}$  vibration modes are also in very good agreement with theoretical prediction (15).



**Figure 4.** The fourth process for chromatographic separation and spectroscopic characterization of fullerenes from the second, additional pyridine extract of *p*-xylene insoluble soot.

The observed unique and the main, dominant C<sub>76</sub> features, relative intensities and locations of all absorption bands in agreement with theoretical predictions (15), as well as mutual agreement of the obtained significant spectra, provide evidence of the presence of purified higher fullerene C<sub>76</sub> in corresponding, mentioned chromatographically separated fractions from the several different separation processes in this research (12–14), including the new process. Better agreement of the experimentally obtained C<sub>76</sub> absorption maxima with theoretical calculations (12–14,15), in comparison to previous results for C<sub>76</sub> (15–17) indicate the advancement in separation and characterization of this molecule in our research.



According to theoretical calculations for the higher fullerene  $C_{84}$ , dominant bands are predicted to occur around  $1600\text{ cm}^{-1}$ , a group (including the main band) between  $1390$  and  $1125\text{ cm}^{-1}$ , and bands around  $840$  and  $630\text{ cm}^{-1}$  (18,19). These findings (18) are in agreement with the original experimentally obtained IR spectra of the isolated molecule of the higher fullerene  $C_{84}$  from the separation processes in this research (12–14), including the new process. In these spectra, a series of four characteristic, sharp, pronounced neighbor bands is registered at  $843$ ,  $780$ ,  $742$  and  $711\text{ cm}^{-1}$ , as well as the second group of sharp bands around  $630\text{ cm}^{-1}$  in the first part of the spectrum significant for  $C_{84}$ . Dominant bands appear around  $1600\text{ cm}^{-1}$ , and a group between  $1390$  and  $1125\text{ cm}^{-1}$ , including the main band, in the second relevant part of the spectrum.

In the previous experimentally obtained IR spectrum of the main chromatographic fraction of  $C_{84}$  fullerene (partially separated isomers), a modest band appears at  $1630\text{ cm}^{-1}$ , a group between  $1432$  and  $1108\text{ cm}^{-1}$ , as well as four bands, two at  $798$  and  $793\text{ cm}^{-1}$  and two at  $648$  and  $635\text{ cm}^{-1}$  in the first relevant part (19). Unlike our results (12–14), the mentioned spectrum (19), and the later obtained spectra of the samples of the two major isomers of fullerene  $C_{84}$ , the  $D_2(\text{IV})$  and  $D_{2d}(\text{II})$  isomers (20), which have similar properties, did not correlate well with the general pattern of the theoretically calculated spectra for  $C_{84}$  fullerene, the  $D_2(\text{IV})$  and  $D_{2d}(\text{II})$  isomers (18). Whereas there is a good correlation of our experimentally obtained IR spectra of the purified molecule  $C_{84}$  (12–14) with theoretical predictions (18), the distinguishing between the  $D_2(\text{IV})$  and  $D_{2d}(\text{II})$  isomers (19) through the use of the predicted IR spectra could not be accomplished (18,19).

All the experimentally obtained locations of absorption maxima of the purified higher fullerene  $C_{84}$  (12–14) are also in agreement with the theoretically calculated IR active vibration frequencies for  $C_{84}$ , by Zhang and coauthors (21). In contrast to previously mentioned spectra of the purified  $C_{76}$  fractions (12–14), the absorption in the central relevant part of the spectrum was not registered. Vibration bands appear in the two distinct regions significant for  $C_{84}$ : the first from approximately  $450\text{ cm}^{-1}$  to  $850\text{ cm}^{-1}$ , and the second from  $1050\text{ cm}^{-1}$  to  $1650\text{ cm}^{-1}$ , which is in general agreement with the previous theoretical and experimental findings for  $C_{84}$  (12, 14, 18–21).

In the obtained UV/VIS spectra of chromatographically purified fractions of the higher fullerene  $C_{76}$  from our research, significant decrease of relative intensities of the dominant absorption bands at  $257$  and  $327\text{ nm}$  is observed in comparison to spectra of the previous purified fullerene fractions,  $C_{60}$  and  $C_{70}$ . The third most intense absorption is moved to the region below  $200\text{ nm}$ . Pronounced  $C_{76}$  shoulder at  $275\text{ nm}$  (12–14), its band at  $405\text{ nm}$  and absorption prolonged to  $900\text{ nm}$  is present. Complete absorption corresponds to  $C_{76}$ , confirming the result of IR characterization of these fractions.

In addition, in the UV/VIS spectra of the obtained purified  $C_{76}$  samples from much diluted hexane solutions, to complete discoloring, that we also recorded for comparison, the absorption maxima were registered at:  $229$ ,  $285$ ,  $327$ ,  $350$ ,  $381$  and  $405\text{ nm}$ . These spectra are in agreement with the UV/VIS spectrum of  $C_{76}$  recorded from very dilute solution in hexane, in the range from  $200$  to  $800\text{ nm}$  (11), but have shown some differences compared with the mentioned spectra of  $C_{76}$  measured from more concentrated solutions in hexane (12–14). With the change of solution concentration, such as significant dilution, the appearance of several new close absorption bands or the fine structure may occur.

The UV/VIS spectra of chromatographically purified fractions of the higher fullerene  $C_{84}$  have shown completely new properties. Pronounced series of absorption maxima unique to the higher fullerene  $C_{84}$  was registered at precisely  $223$ ,  $231$ ,  $236$ ,  $240$ ,  $252$ ,  $261$ ,  $272$ ,  $287$ ,  $304$ ,  $318$ ,  $334$  and  $357\text{ nm}$ . (12–14). A series of very close  $C_{84}$  absorption shoulders is also observed at  $209$ ,  $213$ ,  $217$ ,  $219$  and  $229\text{ nm}$ , as well as intense, sharp

C<sub>84</sub> maximum at 205 nm. All absorption bands in these spectra correspond to carbon cluster C<sub>84</sub>, confirming the result of IR characterization. Complete UV/VIS absorption of the higher fullerene C<sub>84</sub> in the significant region from 200 to 400 nm, here described has not yet been reported under any experimental conditions.

In this study, the UV/VIS spectra of the higher fullerenes C<sub>76</sub> and C<sub>84</sub>, as well as of the basic fullerenes C<sub>60</sub> and C<sub>70</sub>, from hexane solutions of determined concentration in the region from 200 nm to 900 nm, including the significant region from 200 to 400 nm, where fullerenes intensively absorb were presented (12–14), which has not been reported previously for the higher fullerenes. In the work of Jinno et al., the spectra of higher fullerenes recorded from the mixture of acetonitrile and toluene (55:45 or 50:50, v/v), in the range of 300–600 nm, were reported (22,23), while in the study of Kikuchi and coauthors the spectra of higher fullerenes from benzene solutions in the range of 500–1100 nm were presented (24,25). In the articles of Ertle and Diederich et al., the UV/VIS spectra of the molecule C<sub>76</sub> from dichloromethane solutions, in different ranges were presented (16,26). The locations of absorption bands of carbon cluster C<sub>84</sub> in the spectrum obtained from CHCl<sub>3</sub> solution, in the range from 280 to 912 nm, were mentioned in the previous article (11).

In our research, however, characteristic and new properties, the unique and the main, dominant IR and UV/VIS optical absorption maxima of the higher fullerenes C<sub>76</sub> and C<sub>84</sub> were registered in the regions where they intensively absorb, in the obtained original spectra. The IR and UV/VIS spectra of all the isolated C<sub>76</sub> and C<sub>84</sub> samples from the several different separation processes are in good agreement. The results of UV/VIS analysis confirmed the results of IR analysis. Characteristic changes of relative intensities and locations of absorption bands were also observed, showing isolation and separation of the basic and the higher fullerenes in the similar, regular way in different processes.

All the presented results and data indicate the achieved advances in chromatographic separation and spectroscopic characterization of the higher fullerenes C<sub>76</sub> and C<sub>84</sub> in comparison to previous separation processes.

## Conclusion

In the first phase of this research, the basic and the higher fullerenes, mainly C<sub>76</sub> and C<sub>84</sub>, were extracted with the previously unapplied series of solvents and combinations of solvents from the samples of carbon soot produced in electric arc, such as *n*-heptane, toluene, chlorobenzene, *p*-xylene, *o,m,p*-xylenes, pyridine, as well as successively with *p*-xylene and pyridine and with toluene and chlorobenzene. The yields, as well as the compositions of all the obtained extracts, were determined and compared. For the applied series of solvents the series of fullerenes solubility was obtained.

The yields of the obtained *n*-heptane extracts were 0.7%; yields of the toluene extracts were 5.4%. Chlorobenzene extract of the initial soot was obtained in 5.8% yield. The yields of the obtained *p*-xylene extracts were 5.9–6.0%, while the yield of *o,m,p*-xylenes extract was 11.8–11.9%. Pyridine extract of the initial soot was obtained in maximal 16.4% yield due to the original procedure in prolonged time. Applying extraction of the remaining *p*-xylene insoluble soot with pyridine, the second, additional pyridine extract was obtained in 5.9% yield. The entire fullerenes extract yield from this soot sample was increased from 5.9% to 11.8%. Also, by extraction of toluene insoluble soot with chlorobenzene, the second, additional chlorobenzene extract was obtained in 0.4% yield. The entire fullerenes yield from this soot sample was increased from 5.4% to 5.8%.

In comparison to results obtained with *n*-heptane (12) and previously obtained by Kratschmer et al. (1%) (1), significant increases of fullerenes yields and additional

selective extractions of higher order fullerenes were achieved using new procedures with the applied solvents or combinations of solvents (8–10,12–14).

In the second phase of research, the obtained soot extracts were chromatographically separated on the active alumina columns, by continue elution with the several different, original, defined systems of solvents: from pure hexane, or 5% toluene in hexane to pure toluene (12–14), including the new processes with the original system of solvents described in this article. The main progress is the isolation of the purified higher fullerenes  $C_{76}$  and  $C_{84}$ , successively after the basic, by the new improved methods, in one phase of each of the processes, under atmospheric pressure, and smaller flow of 1.5 ml/min, which has not been described previously.

In comparison to previous chromatographic methods for obtaining of these molecules under pressure (22–26), on  $Al_2O_3$  (11), several other advances were realized. The entire material expenses of the work were reduced. Significantly smaller amounts of the initial materials, such as fullerene extract (10 mg), stationary phase, finely granulated  $Al_2O_3$  (50 g), solvent eluent (1.5–1.75 l), per chromatography, as well as cheaper laboratory equipment were used. The entire time of the purification processes was decreased from 16.7 to 19.4 hours. The purified higher fullerenes were obtained in increased milligrams yields. Starting from 10 mg of the soluble soot extract, in average *ca.* 1 mg of  $C_{76}$  and *ca.* 1 mg of  $C_{84}$  in purified form were isolated per one chromatographic process, or up to few milligrams in some cases.

For comparison, using flash chromatography to separate fullerenes required about 50 times larger quantities of the initial materials, such as: 500 mg of crude fullerenes extract, 2500 g of alumina and about 12.5 l of solvent for one chromatographic fraction,  $C_{60}$ , or 75 l for six chromatographic fullerene fractions, per chromatography and the large size of columns. The time of only this phase of the process, initial flash chromatography, was more then 34 hours (11,27). All the obtained four yellowish mixed fractions of the higher fullerenes were then rechromatographed on neutral alumina columns (11). Each of these chromatographies lasted about 8 hours. The entire time of this purification protocol was increased to 66 hours. Purified molecules of the higher fullerenes were obtained in lower yields. From the total amount of 2500 mg of toluene soluble soot extract, 12 mg of  $C_{76}$  and 2 mg of  $C_{84}$  were isolated.

From these data it follows that  $\sim 21$  times larger amounts of the initial materials (extract, stationary phase and solvent), and  $\sim 2$  times longer time is needed for obtaining of 1 g of purified  $C_{76}$ , and  $\sim 125$  times larger amounts of the initial materials and  $\sim 10$  times longer time for obtaining of 1 g of purified  $C_{84}$  by the mentioned flash chromatography process, in comparison to our protocols.

These solutions increase the efficiency of separation of fullerenes, using  $Al_2O_3$  as the stationary phase, optimize and at the same time simplify the method, and overcome the problem of relatively low solubility of fullerenes in a variety of solvents. They exceed technological capabilities of the previous chromatographic methods whereby only the basic fullerenes were successfully isolated and characterized, at ambient conditions.

Moreover, the previous knowledge about capability of alumina in separation of fullerenes (2–11), upon different experimental conditions has been enriched. The results of our investigation, within the several different separation processes, indicated that this important, common, easy available chromatographic material can be employed for successful separation of the basic and the next most abundant higher fullerenes  $C_{76}$  and  $C_{84}$ , upon the adequately chosen, above mentioned experimental conditions, such as: optimal solvent gradients, flow, amounts of the initial materials, etc., already at atmospheric pressure.

All the chromatographically purified fullerene fractions and carbon soot extracts were characterized by determined techniques of IR and UV/VIS spectroscopy that have not been presented previously for the higher fullerenes.

The presence of the higher fullerenes  $C_{76}$  and  $C_{84}$  was already evident in the first three fractions of the second, additional pyridine extract of carbon soot insoluble in *p*-xylene, in mixture. As the main result of this separation process, the presence of purified higher fullerene  $C_{76}$  was indicated in the fourth fraction. The presence of the molecules  $C_{84}$  and  $C_{76}$  was indicated in the fifth fraction, and the presence of purified higher fullerene  $C_{84}$  was indicated in the sixth fraction.

The IR and UV/VIS analyses of the obtained soot extracts, as well as their yields confirmed the results of their chromatographic separations. It was found that pyridine and *o,m,p*-xylenes are suitable and much better solvents than *p*-xylene and *n*-heptane for extraction of higher fullerenes. The selective presence of the higher fullerenes, mainly  $C_{76}$  and  $C_{84}$  was indicated in the second, additional pyridine extract. It was also indicated (6–8) that toluene extracts predominantly fullerene  $C_{60}$  and in considerably less extent  $C_{70}$  from the soot, while chlorobenzene is a suitable solvent both for extraction of  $C_{60}$  and higher order fullerene  $C_{70}$ , and can be used for obtaining fractions enriched by  $C_{70}$ .

The main advancement in spectroscopic characterization of the purified higher fullerenes  $C_{76}$  and  $C_{84}$  from this research is in excellent agreement of all the observed spectroscopic features with theoretical calculations (15,18,19), in the whole relevant spectral region. Another important advancement is the registration of the unique and the main, dominant IR and UV/VIS optical absorption maxima of these molecules in the regions where they intensively absorb, which has not been presented previously.

On the basis of the obtained results, it is concluded that the developed, suitable methods, techniques and processes, with the employed systems of solvents, and  $Al_2O_3$  as the stationary phase material, can be used in practice for obtaining of the basic and the higher fullerenes  $C_{76}$  and  $C_{84}$  of high purities in increased yields, at entirely lower cost, in less time, as well as for their characterization.

These findings will enable easier availability and identification of the mentioned fullerenes for the growing needs of investigation of their remarkable properties, as well as for the numerous possible applications, in for example: electronic and optical devices, magnetic materials, catalysts, fuels, biologically active molecules, diagnostic and therapeutic agents, targeted drug delivery, chemical, optical and bio sensors, polymers, special lenses, early diagnosis of diabetes and so forth (1–5). This is especially important considering that the higher fullerenes  $C_{76}$  and  $C_{84}$  are the next major and the most abundant higher fullerenes after  $C_{60}$  and  $C_{70}$ , and so far the most concerned, the most significant and the most used, as such.

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## References

1. Krätschmer, W., Lamb, L. D., Fostiropoulos, K., and Huffman, D. R. (1990) Solid  $C_{60}$ : A new form of carbon. *Nature*, 347: 354–358.
2. Koruga, Dj., Hameroff, S., Withers, J., Loufty, R., and Sundareshan, M. (1993) Symmetry of electronic and vibrational structure of  $C_{60}$ . Fullerene production. *Electrochemistry of fullerenes*

- and its applications. Practical applications of fullerenes. In *Fullerene C<sub>60</sub>: History, Physics, Nanobiology*, Elsevier Science Publishers: Amsterdam, pp. 83–106, 273–290, 305–368.
- Hirsch, A. and Brettreich, M. (2005) The parent fullerenes. Principles and perspectives of fullerene chemistry. In *Fullerenes Chemistry and Reactions*, Wiley: VCH Verlag GmbH & Co. KGaA: Stuttgart, New York, pp. 1–48, 383–415.
  - Jinno, K. (1999) Technical advances in the liquid chromatographic separation of fullerenes. The preparative separation of fullerenes. In *Separation of Fullerenes by Liquid Chromatography*, RSC Chromatography Monographs, Royal Society of Chemistry: Cambridge, pp. 1–24, 25–48.
  - Taylor, R. (1995) Fullerene production. Properties of fullerenes. In *The Chemistry of Fullerenes*, World Scientific Publishing: London, pp. 20–52.
  - Ajie, H., Alvarez, M. M., Anz, S. J., Beck, R. D., Diederich, F., Fostiropoulos, K., Huffman, R., et al. (1990) Characterization of the soluble all-carbon molecules C<sub>60</sub> and C<sub>70</sub>. *J. Phys. Chem.*, 94: 8630–8633.
  - Bethune, D. S., Meijer, G., Tang, W. C., Rosen, H. J., Golden, W. G., Seki, H., Brown, C. A., and de Vries, M. S. (1991) Vibrational Raman and infrared spectra of chromatographically separated C<sub>60</sub> and C<sub>70</sub> fullerene clusters. *Chem. Phys. Lett.*, 179: 181–186.
  - Jovanovic, T., Koruga, Dj., Jovancicevic, B., and Simic-Krstic, J. (2003) Modifications of fullerenes extractions and chromatographies with different solvents. *Fuller. Nanotub. Car. N.*, 11: 383–394.
  - Jovanovic, T., Koruga, Dj., Polic, P., and Devic, G. (2003) Extraction, separation and characterization of fullerenes from carbon soot. *Mater. Sci. Forum*, 413: 59–64.
  - Jovanovic, T., Koruga, Dj., Jovancicevic, B., and Simic-Krstic, J. (2003) Improvement in separation of nanostructured carbon clusters C<sub>60</sub> and C<sub>70</sub>. *Int. J. Nanosci.*, 2: 129–140.
  - Diederich, F., Ettl, R., Rubin, Y., Whetten, R. L., Beck, R., Alvarez, M., Anz, S., et al. (1991) The higher fullerenes: Isolation and characterization of C<sub>76</sub>, C<sub>84</sub>, C<sub>90</sub>, C<sub>94</sub>, and C<sub>70</sub>O, an oxide of D<sub>5h</sub>-C<sub>70</sub>. *Science*, 252: 548–551.
  - Jovanovic, T., Koruga, Dj., Jovancicevic, B., and Simic-Krstic, J. (2009) Advancement of the process for extraction, chromatography and characterization of fullerenes. *Fuller. Nanotub. Car. N.*, 17: 135–150.
  - Jovanovic, T., Koruga, Dj., Jovancicevic, B., Vajs, V., and Devic, G. (2012) Comparative spectroscopic characterization of the basic and the higher fullerenes. *Fuller. Nanotub. Car. N.*, 21: 64–74.
  - Jovanovic, T., Koruga, Dj., and Jovancicevic, B. (2011) Isolation and characterization of the higher fullerenes from carbon soot. *Fuller. Nanotub. Car. N.*, 19: 309–316.
  - Orlandi, G., Zerbetto, F., Fowler, P. W., and Manolopoulos, D. E. (1993) The electronic structure and vibrational frequencies of the stable C<sub>76</sub> isomer of D<sub>2</sub> symmetry. *Chem. Phys. Lett.*, 208: 441–445.
  - Ettl, R., Chao, I., Diederich, F., and Whetten, R. L. (1991) Isolation of C<sub>76</sub>, a chiral (D<sub>2</sub>) allotrope of carbon. *Nature*, 353: 149–153.
  - Michel, R. H. (1994) Vibrational spectroscopy of purified C<sub>76</sub>. *Ber. Bunsenges. Phys. Chem.*, 98: 975–978.
  - Bakowies, D., Kolb, M., Thiel, W., Richard, S., Ahlrichs, R., and Kappes, M. M. (1992) Quantum chemical study of C<sub>84</sub> fullerene isomers. *Chem. Phys. Lett.*, 200: 411–417.
  - Avent, A. G., Dubois, D., Penicaud, A., and Taylor, R. (1997) The minor isomers and IR spectrum of [84]fullerene. *J. Chem. Soc., Perkin Trans.*, 2: 1907–1910.
  - Dennis, T. J. S., Hulman, M., Kuzmany, H., and Shinohara, H. (2000) Vibrational infrared spectra of the two major isomers of [84]fullerene: C<sub>84</sub>{D<sub>2</sub>(IV)} and C<sub>84</sub>{D<sub>2d</sub>(II)}. *J. Phys. Chem., B*, 104: 5411–5413.
  - Zhang, B. L., Wang, C. Z., and Ho, K. M. (1993) Vibrational spectra of C<sub>84</sub> isomers. *Phys. Rev. B*, 47: 1643–1646.
  - Jinno, K., Matsui, H., Ohta, H., Saito, Y., Nakagawa, K., Nagashima, H., and Itoh, K. (1995) Separation and identification of higher fullerenes in soot extract by liquid chromatography-mass spectrometry. *Chromatographia*, 41: 353–360.

23. Jinno, K., Sato, Y., Nagashima, H., and Itoh, K. (1998) Separation and identification of higher fullerenes by high performance liquid chromatography coupled with electrospray ionization mass spectrometry *J. Microcolumn. Sep.*, 10: 79.
24. Kikuchi, K., Nakahara, N., Honda, M., Suzuki, S., Saito, K., Shiromaru, H., Yamauchi, K., et al. (1991) Separation, detection and UV/visible absorption spectra of fullerenes: C<sub>76</sub>, C<sub>78</sub> and C<sub>84</sub>. *Chem. Lett.*, 20: 1607–1610.
25. Kikuchi, K., Nakahara, N., Wakabayashi, T., Honda, M., Matsumiya, H., Moriwaki, T., Suzuki, S., et al. (1992) Isolation and identification of fullerene family: C<sub>76</sub>, C<sub>78</sub>, C<sub>82</sub>, C<sub>84</sub>, C<sub>90</sub> and C<sub>96</sub>. *Chem. Phys. Lett.*, 188: 177–180.
26. Diederich, F. and Whetten, R. L. (1992) Beyond C<sub>60</sub>: The higher fullerenes. *Acc. Chem. Res.*, 25: 119–126.
27. Tour, J. M., Scrivens, W. A., and Bedworth, P. V. (1997) Purification of fullerenes, U.S. Patent 5,662,876.