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# Filtration process combined with mechanical action, as a method for efficient extraction of endohedral metallofullerenes from carbon soot

Victoria I. Elesina<sup>a,b</sup>, Grigory N. Churilov<sup>a,b</sup>, Natalia G. Vnukova<sup>a,b</sup>, Alexander I. Dudnik<sup>a,b</sup>, and Irina V. Osipova<sup>a</sup>

<sup>a</sup>FSBSI "Federal Research Center "Krasnoyarsk Science Center SB RAS", Krasnoyarsk, Russia; <sup>b</sup>Siberian Federal University, Institute of Engineering Physics and Radio Electronics, Krasnoyarsk, Russia

## ABSTRACT

The paper presents results of fullerenes and endohedral metallofullerenes extracts studies, isolated from the graphite rods carbon soot spray, and containing  $Y_2O_3$  in a high frequency arc discharge. Two ways of extraction were applied and compared – (1) the classic method of Soxhlet extraction, and (2) the one developed by our team – extraction based on mechanical action combined with filtration. To implement the method, we used a laboratory version of installation, embodying technical solutions for rapid extraction. Chromatographic and mass spectrometry studies of fullerene extracts obtained by these methods revealed that by combining mechanical action with simultaneous filtration, we can significantly intensify and reduce the process of extracting fullerenes and endohedral metallofullerenes compared to the Soxhlet extraction method. This is especially evident in the release of endohedral metallofullerenes. Our method allows to reduce the release time of fullerenes from 10 g of carbon soot on laboratory installation up to 15 minutes, against the Soxhlet extraction method taking 18 hours. Whilst, the total number of fullerenes extracted by both methods almost coincides (the extraction method using mechanical action allowed us to extract 0.2–0.4 wt. % more), the composition of the isolated fullerene mixtures is different. The relative content of higher fullerenes and endohedral metallofullerenes exceeds when the mechanical action-based extraction method applied.

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## KEYWORDS

Fullerenes; solvent extraction; mechanical extraction; Soxhlet; turbulent flow

## 1. Introduction

Fullerenes are important for their remarkable properties. It is known that when carbon salts or metal oxides are introduced in the process of synthesis in addition to fullerenes, carbon soot also contains endohedral metallofullerenes (EMF). There are numerous possible applications for these materials. Numerous studies have shown that on the basis of fullerenes and EMF, also true when their derivatives applied, you can successfully solve problems in the field of chemistry, radio electronics, energy, materials science, environmental studies, medicine.<sup>[1–3]</sup> Fullerenes and EMF can be particularly effective when used in photovoltaic devices,<sup>[4]</sup> as electroactive components for energy devices,<sup>[5]</sup> as components of adsorbents,<sup>[6]</sup> and can also as a base for developing medicine, or as contrast agents in tomography,<sup>[7]</sup> etc.

Despite the fact that many methods have been developed<sup>[8–10]</sup> and devices for fullerenes and EMF extraction from carbon soot, obtained by spraying graphite rods in an arc discharge in a helium atmosphere,<sup>[11]</sup> there is no universal method that allows to quickly and efficiently isolate them. Studies of multiple research groups have shown that the difficulty of isolating EMF is due to strong Van der Waals bonds of both fullerenes between themselves and the

insoluble component of carbon soot.<sup>[12]</sup> Fullerene clusters are tens of nanometers in size, and clusters in which higher fullerenes and EMF are present are hundreds of nanometers.<sup>[13,14]</sup> By placing carbon soot in a non-polar solvent, only an insignificant part of fullerenes will dissolve, most will remain bound to the solid insoluble component of soot (particles of fine graphite, graphenes, nanotubes, etc.). Researchers use multiple flooding of carbon soot with solvent<sup>[1,15,16]</sup> to isolate fullerenes, for which the Soxhlet extraction method and Soxhlet apparatus<sup>[17]</sup> are most frequently applied. The method of extraction by Soxhlet is based on the fact that with each new extraction cycle, the solvent evaporates and condenses on the reflux condenser, after which it flows into the filtering tube. When filling the filtering tube, the solution is poured into the original flask, gradually transporting the solute through the wall of the filtering tube. When this occurs, multiple sorption and desorption by the stationary phase, i.e. carbon soot particles occur. Only when the solution overcomes the filtering tube in which the carbon soot is located and flows into the flask, the subsequent sorption is excluded.

The method of extraction based on mechanical action combined with filtration (method of mechanical extraction) developed and applied by our team<sup>[18]</sup> is based on the fact

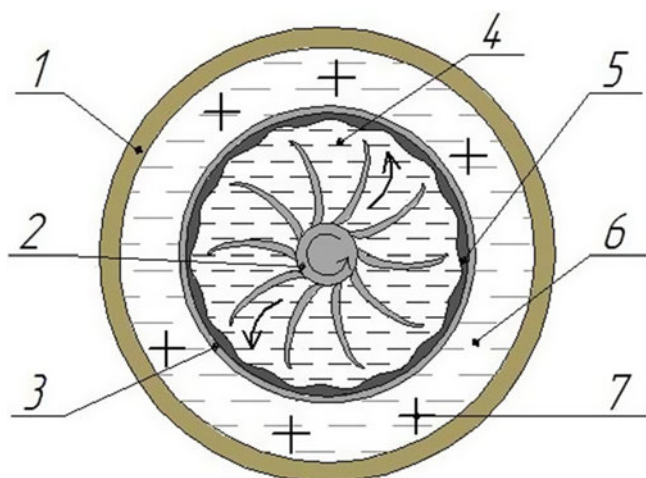


Figure 1. Extractor drawing (top view, cover not shown).<sup>[18]</sup>

that carbon soot with rotating blades of a specially developed laboratory variant of the installation (extractor) is mechanically mixed and applied to the inner surface of the filtering tube, forming a thin layer at the interface. The flow of non-polar solvent under the action of centrifugal force in a thin layer of carbon soot quickly dissolves fullerenes and carries them through the wall of the filtering tube. The applied method speeds up the mass transfer and significantly shortens the extraction time. The mechanical effect on a thin layer of carbon soot is combined with simultaneous filtration, which significantly reduces the re-sorption of fullerenes by soot particles. This allows to achieve a positive effect – quick and effective release of fullerenes.

The present work keeps on coverage of the research on isolation of EMF containing fullerenes mixture aiming for higher efficiency of extraction. The study is conducted by the method developed by our group and also by the method of Soxhlet extraction, and is a continuation of our previous studies.<sup>[18]</sup>

The properties of EMF are significantly different from the properties of ordinary fullerenes, respectively, the release of EMF also differs. Studies presented in this work have shown that the application of our method is effective for the isolation of EMF.

## 2. Experimental

Carbon soot was obtained by sputtering graphite electrodes in an high frequency arc discharge.<sup>[19]</sup> The high-frequency arc discharge setup<sup>[19]</sup> operates in a helium atmosphere and is used to syntheses carbon soot with different dispersion and structure, along with fullerenes and EMF. An axial hole 3 mm in diameter was drilled at the electrodes (TC 3497-001-51046676-2008, diameter 6 mm, length 100 mm) and filled with a mixture of graphite powder and  $Y_2O_3$  50 wt. % each.

The resulting carbon soot was extracted in the Soxhlet apparatus and in the extractor (Figure 1), which consists of a cylindrical body (1) and a shaft with blades (2), rotating inside the case by means of an engine. The blades are located on the shaft (2) at an equal distance from each other and are somewhat curved in an arc. Inside the shaft there

are openings through which the suspension enters the separation chamber (4) located inside the filtering tube (3). The filtering tube (3) is installed between the shaft with the blades (2) and the inner wall of the housing. The cylindrical body (1) is equipped with a lid with a loading port for feeding the suspension. The structure and principle of operation of the extractor are described in detail in.<sup>[18]</sup>

To isolate fullerenes by our method, a suspension was prepared by mixing carbon soot with solvent for 3-5 minutes at the rate of 100 ml per 1 g. The suspension was supplied from the outside into the gap between the shaft with blades (2) and the wall of the filtering tube. A turbulent slurry flow was created inside the separation chamber (4) by moving blades located on the shaft (2). In the extraction process, another 100-150 ml of solvent was added to the extractor until the color of the resulting fullerene solution disappeared. In the course of the extraction, the suspension was divided into a solid component (5), which was distributed in a thin layer on the inner wall of the filtering tube and its bottom, and a solution of fullerenes (6). The fullerene solution flowed into the receiving vessel under the cylindrical body (the direction of flow of the fullerene solution is perpendicular to the plane of the figure and is shown with the arrows (7)).

For the extraction of fullerenes by the method of Soxhlet extraction, carbon soot was directly loaded into the filtering tube, from which fullerenes were released. The method is well-known and well described in the literature.<sup>[17,18]</sup> All the extractions run by the two compared methods were carried out using carbon disulfide ( $CS_2$ ), one of the effective fullerene solvents,<sup>[20-22]</sup> most often used for the complete extraction of fullerenes, including EMF.

Mass spectra of the samples were recorded with a Bruker Autoflex mass spectrometer with laser desorption. Studies by high performance liquid chromatography (HPLC) were carried out on an Agilent 1200 Series chromatograph with a data processing system and an output of analysis results. The chromatograph is equipped with a Buckyprep-M column (10 × 250 mm). The flow rate of toluene as eluent was 5 ml/min. The wavelength of the UV detector was 324 nm. The samples were weighed on an AND GH-252 electronic scale.

To isolate fullerenes from the original carbon soot, all the synthesized soot was divided into 6 parts of 10 g each, 3 of which were subjected to Soxhlet extraction by the method, the other 3 by the method of mechanical extraction. A comparative analysis yielded results similar in the number of isolated fullerenes. The method of mechanical extraction was allocated 5.2 (±0.1) wt. % fullerenes, and the method of extraction of Soxhlet – 5.0 (±0.1) wt. %.

The extraction of fullerenes by the method of mechanical extraction was carried out at room temperature for no more than 15 minutes, including sample preparation (direct separation of the suspension occurred in 4-5 minutes). Processing of each sample by the method of Soxhlet extraction took 18 hours. The composition of the isolated fullerene mixtures was different. The fullerene mixture isolated in the extraction unit using the Soxhlet apparatus contained fewer higher fullerenes and EMF than the fullerene mixture extracted by

the extractor. Chromatographic spectra of the obtained samples are presented in Figure 2.

In order to test the extractor work efficiency on the extraction of EMF from carbon soot, processed by the method of Soxhlet extraction, repeated extraction of fullerenes was carried out via the mechanical extraction. For this purpose, 3 samples of carbon soot were synthesized in line with the above method procedure.<sup>[19]</sup> Each of the obtained samples with a mass of 10g was first processed by the Soxhlet's extraction method on an extraction unit using a Soxhlet apparatus. Then, the soot remaining after the extraction with the Soxhlet apparatus was dried and subjected to repeated treatment by the method of mechanical extraction in an extractor.

All extractions were also carried out with carbon disulfide application. The time spent on the using of the methods of Soxhlet extraction and mechanical extraction, as in the above case, was 18 hours and 15 minutes, respectively. The resulting solutions of fullerene extracts were thoroughly filtered; the solvent was distilled off on a rotary evaporator. After drying, the solid samples of fullerene mixtures were obtained, which, for convenience, we designated as FM1 (samples of fullerene mixtures separated by Soxhlet extraction from the original carbon soot) and FM2 (samples of

fullerene mixtures extracted by the repeated extraction with a method of mechanical extraction from carbon soot, processed by Soxhlet extraction method).

### 3. Results and discussion

The relative content of FM1 in carbon soot obtained was 5.0 ( $\pm 0.1$ ) wt. %, and FM2 – 0.4 ( $\pm 0.1$ ) wt. %. This result is quite interesting, because it is not obvious and shows that repeated mechanical extraction is more efficient than the extraction with the Soxhlet apparatus alone.

The HPLC method was used to separate all obtained samples of fullerene mixtures (FM1 and FM2) into fractions, the percentage ratio of the relative content of different fullerenes in these fractions was determined after weighing them (see Table 1 below).

The results of the study of fullerene mixtures by HPLC are shown in Figure 3.

Mass spectrometry studies of fullerene mixtures are shown in Figure 4.

Since the difference in the results of measurements of all samples of each fullerene mixture (both FM1 and FM2) did not differ by more than 0.1 wt. %, Table 1 shows the average measurement values, rounded to 0.1. The spectra of the chromatograph and mass spectrometer of all samples of each fullerene mixture (both FM1 and FM2) were identical, therefore, the article presents the results of HPLC and mass spectrometry of one typical sample from each type of fullerene mixtures (one of FM1 and one of FM2).

An interesting fact is that with the extraction by Soxhlet extraction and mechanical extraction, the difference in the amount of fullerenes extracted from carbon soot made only 0.2 wt. % (5.0 and 5.2 wt. %, respectively). At the same time, the method of mechanical extraction from carbon soot already treated with the Soxhlet extraction method, was additionally isolated with 0.4 wt. % fullerenes, which contained a significant amount of higher fullerenes and EMF (25 wt. %). Thus, the fourth part of the fullerene mixture, separated by mechanical impact from the carbon soot treated with the Soxhlet extraction method, is enriched with higher fullerenes and EMF. This is an advantage over the previously obtained experimental results.

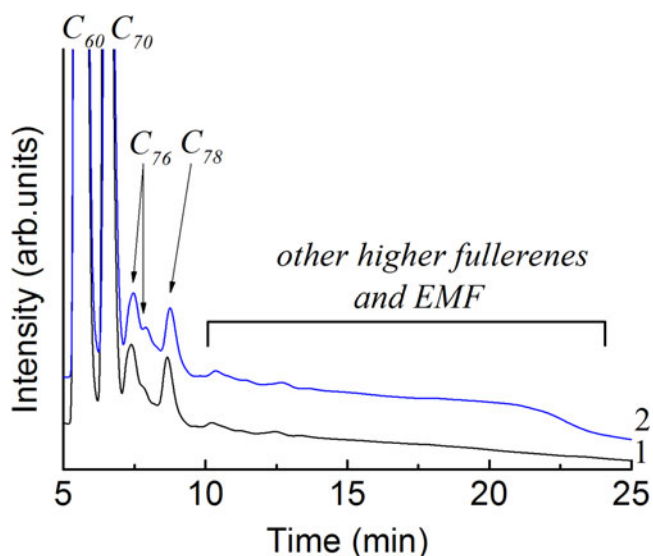


Figure 2. Chromatograms of samples of fullerene mixtures, isolated on the Soxhlet apparatus (1) and on the extractor (2).

Table 1. Various fullerenes fractions in FM1 and FM2 extracts, wt. %.

Method for isolating fullerene mixtures	The relative content of fullerene mixtures in carbon soot		The relative content of fullerenes of different types in fullerene mixtures			The relative content of EMF with Y in fullerene mixtures
			C <sub>60</sub>	C <sub>70</sub>	Higher fullerenes and EMF C <sub>n</sub> , where n ≥ 76, EMF	
Extraction with the Soxhlet setup (FM1)	5.0		69.0	19.0	12.0	4.2
Mechanical extraction after the extraction with the Soxhlet setup (FM2)	5.4	0.4	52.0	23.0	25.0	1.5

\*Standard deviation of the measurement values was  $\pm 0.04 - \pm 0.06$ .

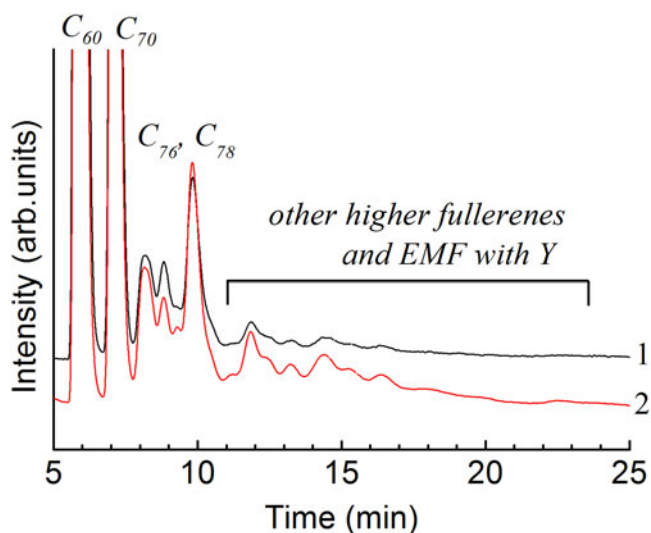


Figure 3. Chromatograms of FM1 (1), FM2 (2) samples.

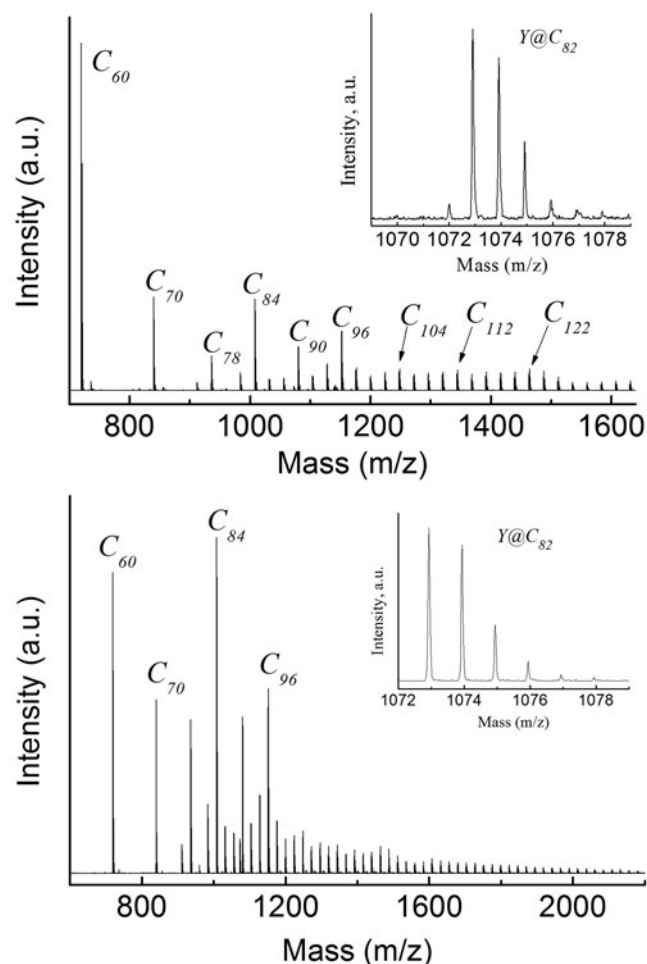


Figure 4. Mass spectra of samples of FM1 (A), FM2 (B).

#### 4. Conclusions

The conducted studies have shown that, relative to the weight of the initial carbon soot, the percentage content of the selected FM1 and FM2 was 5 and 0.4 wt. %, respectively. Thus, we have experimentally established that the use of

only one method of the Soxhlet extraction in the separation of fullerenes and EMF from carbon soot does not provide a complete extraction. Only one part of the fullerenes is extracted by the Soxhlet extraction method, and the fullerene mixture, which is largely enriched with higher fullerenes and EMF, can still be isolated by the additional mechanical extraction from the same carbon soot sample.

This proves the effectiveness of the mechanical extractor and the extraction method proposed on its basis, as well as the fact that, if necessary, the extraction of higher fullerenes and EMF in the preparative amounts, it is efficient to use the Soxhlet apparatus with the subsequent additional release on the extractor.

The work also shows that the extraction of fullerene mixtures containing EMF by the method of mechanical extraction can be carried out in a substantially short time period. The extractor releases fullerenes 20 times faster than the Soxhlet setup set alone, thus, saves the solvent and time for the research work.

In the future, we plan to develop the separation method proposed in the work by increasing the intensity of the mechanical effect on the carbon soot layer and the solvent flow rate.

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