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# Mechanical activation of fullerene containing soot during extraction of higher and endohedral metallofullerenes

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## ABSTRACT

For extraction of higher fullerenes and endohedral metallofullerenes (EMF) with yttrium from fullerene-containing carbon soot (soot) obtained by combined spraying of graphite and yttrium oxide powders in an arc plasma, we developed a device (Extractor\*) that provides mechanical activation effects on agents combined with filtration. It has been shown that the soot recovery percentage of a mixture of higher fullerenes and EMF with different solvents (carbon disulfide, o-xylene, pyridine) and the EMF mass fraction in the mixture is significantly higher than in the extraction with a Soxhlet apparatus traditionally used for these purposes. The time spent on the extraction process is reduced significantly. Due to a known reaction with titanium chloride (TiCl<sub>4</sub>) and removal of a solution of empty fullerenes, subsequent bonding of EMF with yttrium into an insoluble complex directly in the extractor allows the product to be significantly enriched with EMF. In general, we were able to significantly reduce both the duration of extraction of the fullerenes mixture and EMF and the production of EMF separately.

## HIGHLIGHTS

1. A mechanical extractor (Extractor\*) developed by us, which allows processing a larger amount of carbon black and, accordingly, extracting more fullerenes per unit of time, has been applied.
2. The percentage of extraction from the soot of a mixture of higher fullerenes and EMF with various solvents was significantly higher than with extraction using the Soxhlet apparatus.
3. It has been shown that mechanical extractor using makes it possible to increase the coefficient of mass transfer from the surface of the particles to the extracting agents.
4. The Extractor\* was first used for the non-HPLC separation of endohedral metallofullerenes with TiCl<sub>4</sub>. The use of the new device made it possible to isolate a product significantly enriched in endohedral metallofullerenes.

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Fullerenes; endohedral metallofullerenes; extraction; enrichment; titanium chloride

## 1. Introduction

Analysis of literary data showed that endohedral metallofullerenes (EMF) in recent years are particularly intensively investigated for use in various applications: pharmacology, medicine,<sup>[1,2]</sup> ecology,<sup>[3]</sup> electronics and optoelectronics,<sup>[4–6]</sup> and others.<sup>[7–9]</sup> In general, EMF is synthesized by plasma-chemical methods, by co-evaporation of graphite and oxides or metal nitrides.<sup>[10]</sup> However, the production of EMF in macro quantities remains relevant. Existing methods for isolating fullerenes from fullerene-containing soot (hereinafter referred to as soot) based on extraction are not effective enough. EMF is particularly difficult to isolate because it tends to form solvates (molecular complexes with solvents).<sup>[11–13]</sup> The aggregation/disaggregation processes of fullerenes and their derivatives in many solvents have been described.<sup>[14–17]</sup> The sizes of fullerene clusters in which there

are higher fullerenes and EMF can reach hundreds of nanometers.<sup>[18]</sup>

In addition to the long-term method of chromatographic enrichment of the fullerene mixture containing EMF, as well as enrichment via chemical oxidation-reduction methods represented by single works,<sup>[19,20]</sup> the enrichment method associated with complexing agents is popular. Due to its speed and efficiency, the most commonly used is Lewis acid (TiCl<sub>4</sub>). The method is based on the formation of TiCl<sub>4</sub>-metallofullerene complexes, which easily decompose when treated with water, forming a mixture of EMF in neutral form. The papers<sup>[21,22]</sup> describe the potential for EMF release up to > 99% purity for 10 minutes without the use of chromatography.

The purpose of this work is the development of effective techniques for the isolation of fullerenes from carbon soot,

which allows obtaining mixtures enriched with EMF in macro quantities.

Earlier in our studies, Refs. Churilov et al. (2019) and Elesina et al. (2019)<sup>[23,24]</sup> for extraction of fullerenes from carbon soot, for the first time, we used a specially designed device using mechanical activation carbon soot with simultaneous filtration.<sup>[23,24]</sup> In paper,<sup>[23]</sup> this device was used to isolate empty fullerenes with benzene and carbon disulfide. Paper<sup>[24]</sup> contains the results of experiments on the isolation of carbon disulfide fullerenes  $C_{60}$ ;  $C_{70}$ ;  $C_n$ , where  $n \geq 76$  and endohedral metallofullerenes with Y.

Data on the study of the isolation processes of higher fullerenes and EMF by other organic solvents in the literature is limited. The studies are mainly devoted to the isolation of fullerenes  $C_{60}$  and  $C_{70}$ .<sup>[25–27]</sup>

For the reasons given above, the study and introduction of new devices and methods of isolation and enrichment are relevant. The design of the above-mentioned device<sup>[23,24]</sup> has been modernized for research. Since the intensity of mechanical action of the rotating blades on the carbon soot was not sufficient, modernization was needed. Increasing the intensity of the action by reducing the gap between the blades and the filter element and increasing the rotational speed led to rapid wear of the filter element. Our new device (hereinafter Extractor\*) is devoid of these disadvantages, patent<sup>[28]</sup> has been obtained. Extractor\* was tested via isolating a mixture of empty fullerenes and EMF with Y from the soot. Selected solvents were used: carbon disulfide, o-xylene, pyridine. Also directly in Extractor\* EMF was bound into an insoluble complex with  $TiCl_4$ <sup>[21]</sup> to separate them from empty fullerenes dissolving in organic solvents.

Studies of fullerene extraction processes are interesting both from fundamental research and from applied studies perspectives. They will allow the development of methods for the production of fullerenes in macro quantities.

## 2. Experimental section

### 2.1. Production of carbon soot containing fullerenes and EMF with Y

To experiment, we took carbon soot obtained by spraying graphite electrodes in an arc plasma.<sup>[29]</sup> An axial hole 3 mm in diameter was drilled at the electrodes (graphite rods for atomic emission spectral analysis TC 3497-001-51046676-2008, diameter 6 mm, length 100 mm) and filled with a mixture of graphite powders and  $Y_2O_3$  in a mass ratio of 1:1. The rods were pre-annealed in a vacuum at a temperature of 1800°C.

### 2.2. Isolation of a fullerenes mixture and EMF with yttrium from fullerene-containing soot via extraction with organic solvents

In the course of the research, the separation of a mixture of empty fullerenes and EMF with yttrium from carbon soot was carried out according to the Soxhlet method (Soxhlet apparatus was used) and on the Extractor\* we developed. A

detailed description of the design and principle of action is given in ref. Churilov and Elesina (2021).<sup>[28]</sup> The Extractor\*'s body is made rotating about an axis, with magnets installed in the entire volume of its wall. Inside the filter element, there is a cylinder on the surface of which there are metal balls driven by magnets. In Extractor\* fullerenes are isolated from a thin layer of carbon soot while in the Soxhlet apparatus fullerenes are isolated from a large amount of carbon soot and without mechanical phase mixing.

As solvents, carbon disulfide, o-xylene and pyridine were used. Carbon soot was divided into 3 equal parts, which were treated with these solvents at room temperature simultaneously in the Soxhlet apparatus and the Extractor\*. For this, each of the 3 parts of carbon soot was divided into 2 more equal parts.

Extraction of fullerenes using the Soxhlet apparatus was carried out according to standard technology.<sup>[30]</sup> To isolate the fullerenes using Extractor\*, a suspension of carbon soot and the corresponding solvent was prepared at the rate of 100 ml per 1 g. The resulting suspension was fed to Extractor\* and mechanically stirred for 3-5 minutes. The rotation speed of the Extractor\*'s body was 120-300 rpm. The solid component of the suspension was dispersed in a thin layer over the inner surface of the filter element. At the same time, the fullerene solution was filtered and drained to the receiver.

To test the reproducibility of the results on each device, experiments on the isolation of fullerenes were carried out three times. Soot obtained under similar conditions was used.

### 2.3. Production of fullerene mixture enriched with EMF

In the Extractor\* by means of mechanical activation, we bonded EMF into an organic-insoluble complex with  $TiCl_4$  to separate EMF and empty fullerenes, similarly to the known in the literature methods.<sup>[21]</sup>

A solution of empty fullerenes and EMF mixture of about 30 ml, obtained in the Extractor\* from soot with disulfide carbon (see item 2.2), was reintroduced into the Extractor\* and 0.5 ml of  $TiCl_4$  was added. After stirring for 3-5 minutes and adding another 20 ml of carbon disulfide, the solution was filtered through the filter element automatically.

The sedimented  $TiCl_4$ -EMF complex remained on the inner surface of the filter element and was washed with acetone (15 ml). Then ice deionized water was introduced into Extractor\*. The solution with the components of the complex decomposed in water (on EMF and  $TiCl_4$ ) was drained to the receiver. Carbon disulfide was passed through the EMF sediment remaining on the filter element. The resulting solution was poured into the same receiver until the yellow color disappeared. In the resulting mixture of carbon disulfide and water, fullerenes and  $TiCl_4$  were partitioned into immiscible organic and aqueous solutions respectively. Which were further separated by decantation. The procedure lasted 5–7 minutes.

**Table 1.** Percentage comparison of different fullerenes isolated from carbon soot samples with selected solvents using Soxhlet apparatus and Extractor\*.

Solvent	Apparatus	Content of different fullerene types, %			
		C60	C70	C <sub>n</sub> (70 < n ≤ 84)	C <sub>m</sub> (m > 84)+ EMF with Y
carbon disulfide	Extractor*	67.15	21.03	5.63	6.19
	Soxhlet apparatus	67.46	21.68	6.52	4.34
o-Xylene	Extractor*	71.29	22.17	4.35	2.19
	Soxhlet apparatus	72.68	23.63	2.61	1.08
pyridine	Extractor*	79.51	15.23	1.20	4.06
	Soxhlet apparatus	78.75	18.92	2.22	0.11

## 2.4. Analytical studies

All the obtained solutions of fullerene mixtures were filtered, the solvent was distilled off on a rotary evaporator RV 8, IKA (Germany).

Fullerene mixtures were separated by high-performance liquid chromatography (HPLC) on an Agilent-1200 chromatograph with a Cosmosil Buckyprep-M column (10 mm × 250 mm). Toluene was used as eluent and the flow rate was 1.6 ml/min.

The quantitative content of various fullerenes in the extract was evaluated by HPLC chromatograms. The relative content of a particular component in the mixture was calculated by normalizing the area of each peak for Mechanical the total area of the entire spectrum on a chromatogram. For this, a specially developed software algorithm was used. The program performed numerical integration of the spectrum using a trapezoidal method with a linear approximation to account for the background.

In addition, all EMF mixtures obtained were analyzed by atomic emission spectroscopy. Based on the obtained results, the number of EMF with Y was calculated according to the method developed by us.<sup>[31]</sup>

## 3. Results and discussion

### 3.1. Results of extraction of fullerenes and EMF with Y

The results of the fullerene extraction with carbon disulfide, o-xylene, and pyridine by HPLC analysis of the samples are shown in Table 1 and the typical general chromatograms in Figure 1. The standard deviation of the measurement values presented in the table was ± 0.04 – ± 0.06.

When the whole mixture of fullerenes was separated from the soot by mechanical extraction with the selected solutions, an increase in the percentage yield (wt.%) was observed compared to the Soxhlet extraction. It was insignificant and did not exceed 0.2 wt.%.

However, it can be seen from Table 1 that mixtures of fullerenes obtained by mechanical extraction with all selected solvents contained a higher % of higher fullerenes and EMF.

The behavior of the fullerene extract on the Cosmosil Buckyprep-M column is well presented in the literature<sup>[32,33]</sup> and studied by us using the mass spectrometry method. This made it possible to correlate the peaks on the chromatogram with individual molecules of fullerenes.

The combined application of analytical methods (HPLC and atomic emission spectroscopy<sup>[31]</sup>) made it possible to

establish the quantitative content of EMF in fullerenes mixtures obtained from soot with carbon disulfide, o-xylene, and pyridine, using Extractor\* and Soxhlet apparatus.

Using carbon disulfide, the highest amount of C<sub>m</sub> (m > 84) and EMF with Y was isolated by both Extractor\* (6.19%) and Soxhlet apparatus (4.34%). Extraction with o-xylene of 2.19% and 1.08%, respectively, is less effective. The use of pyridine produced an interesting result. It was almost impossible to isolate C<sub>m</sub> (m > 84) and EMF with Y on the Soxhlet apparatus. At the same time, we obtained 4.06% on the Extractor\*.

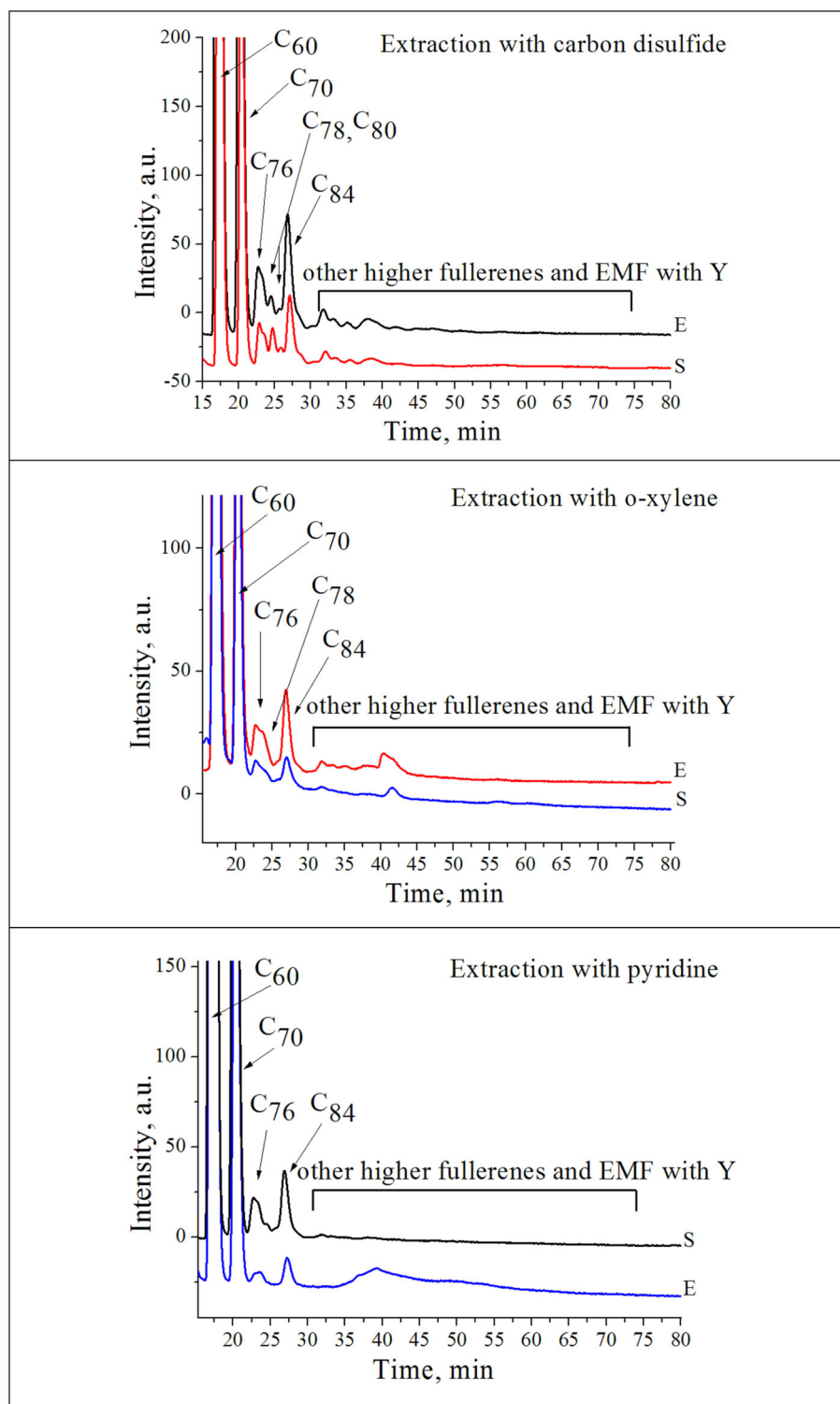
As a result, it was shown that the mixture of fullerenes isolated via extraction from soot using mechanical action is significantly enriched with higher fullerenes and EMF. It should be noted that the time spent separating fullerenes from soot using Extractor\* was 15 minutes and using Soxhlet apparatus from 12 to 16 hours.

### 3.2. Results of enrichment of fullerene mixture containing EMF with Y using Lewis acid (TiCl<sub>4</sub>)

Samples (Table 2) obtained during the separation procedures of EMF and empty fullerenes conducted using Extractor\* were certified via HPLC. Mechanical activation was carried out on the fullerenes and EMF mixture solution, during the binding reaction of EMF into an insoluble complex with TiCl<sub>4</sub>,<sup>[21]</sup> followed by removal by filtration of empty fullerenes. According to the results of the analysis, the filtrate (fraction Fr 1) contains 0.4% EMF with yttrium, but this is significantly less than (1.3%) than in the original sample (fraction Fr 0). In contrast, the fraction Fr 2, resulting from the decomposition of TiCl<sub>4</sub>-EMF, contains 9.4% EMF with yttrium. This corresponds to a significant enrichment of the fullerenes mixture with EMF with yttrium. We were unable to completely carry out the separation of empty fullerenes and EMFs. However, we believe that with the use of Extractor\* this is theoretically possible by increasing the mixing time of the reagents.

## 4. Conclusions

The paper presents the results of studies of the fullerene mixtures composition isolated by extraction with carbon disulfide, o-xylene, pyridine from fullerene-containing soot obtained by the spraying of graphite and yttrium oxide powders in an arc plasma via HPLC and atomic emission spectroscopy.



**Figure 1.** Chromatograms corresponding to the mixtures with the highest EMF content: E – is the sample of the mixture isolated on the Extractor\*; S – is the sample isolated on the Soxhlet apparatus.

**Table 2.** The relative content of different types of fullerenes in the fullerenes mixture solution and EMF with Y.

Fullerene type (Ful)		Fr 0, %	Fr 1, %	Fr 2, %
C60	Cn, where $60 \leq n \leq 80$	$67.4 \pm 0.1$	$55.6 \pm 0.1$	$60.9 \pm 0.1$
C70		$23.2 \pm 0.1$	$31.7 \pm 0.1$	$14.6 \pm 0.1$
C76		$2.2 \pm 0.1$	$2.9 \pm 0.1$	$1.7 \pm 0.1$
C78		$0.8 \pm 0.1$	$1.8 \pm 0.1$	$2.5 \pm 0.1$
C80		$0.2 \pm 0.1$	$0.6 \pm 0.1$	$1.3 \pm 0.1$
C84	Ful (Cn, where $n > 80$ ) + EMF with Y	$3.1 \pm 0.1$	$5.15 \pm 0.1$	$3.2 \pm 0.1$
other Ful		$1.9 \pm 0.1$	$2.0 \pm 0.1$	$6.5 \pm 0.1$
Ful + EMF with Y		$1.3 \pm 0.1$	$0.4 \pm 0.1$	$9.4 \pm 0.1$

When using the mechanical activation on fullerene-containing carbon soot in the isolation process in our specially developed device - Extractor\*, a higher yield of higher and endohedral metallofullerenes (Cm ( $m > 84$ ) and EMF with Y) was observed compared to traditional isolation with the same solvents in the Soxhlet apparatus. Thus, using carbon disulfide in Extractor\*, the largest amount of fullerenes was obtained (6.19%). Using *o*-xylene made it possible to get a good result and extract 2 times more fullerenes (2.19%) on the Extractor\* than on the Soxhlet apparatus (1.08%). The use of pyridine showed interesting results. Fullerenes were almost not isolated on the Soxhlet apparatus. However, Extractor\* isolated 4.06%.

The use of the Extractor\* allowed to isolate a mixture of fullerenes from soot with high EMF content, in a single technological cycle and with less time spent (less than 0.5 hours) compared to traditional methods (12-16 hours). Moreover, it allowed to subsequently remove the main amount of the empty fullerenes for additional enrichment of the fullerene mixture solution with the EMF contained in it.

This shows that using Extractor\* increases the mass transfer ratio from the surface of the particles to the solvent and extracts more fullerenes per unit time.

### Availability of data and material (data transparency)

Not applicable. The authors confirm that the data supporting the findings of this study are available within the article.

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### Disclosure statement

No potential conflict of interest was reported by the authors.

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