PURITY ANALYSIS OF TRADE PRODUCED C-60 FULLERENE

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Abstract. The article compares the product purity of fullerene C-60, synthesized in different laboratories. The content of main product impurities was determined by liquid chromatography, infrared spectroscopy and mass spectrometry. It is shown that only one method of chromatographic analysis, the results of which are given in the certificates of goods, is not enough for detecting detect impurities.

1. Introduction

In the near future the use of nanomaterials, in particular fullerenes, is planned for commercially obtaining heavy-duty composite materials with matrix of plastic or metals. Similar materials will be used also in the most various areas: manufacturing the most important details subjected wearing action for railway transport, mechanical engineering and instrument making; strong and antibacterial packing materials for food industry; in metallurgy, mining industry, coal washing, oil and gas extraction industries, power systems, water-power engineering for creation of the equipment working in hostile environments at high and low temperatures.

The only obstacle for using fullerenes in the area mentioned above and many other areas of technical application is that their production on an industrial scale up to now is a very complex problem which demands huge expenses. Trying to solve this problem, in different laboratories working around the world, considerable advances have been made. The largest manufacturers are: Belgium (Nanocyl S.A.), France (Nanoledge, CNRI, Arkema), England (Thomas Swan, Dynamics Lab.), Germany (Bayer), the USA (Carbon Nanotechnologies, Hyperion Catalysis, Ebay, NanoLab, CarboLex, MER, Tailored Materials Corp., SWeNT, prepared for manufacture Nano-C, MIT), China (Shenzhen Nanotech, GZEnergy, Sunnano), Japan (Showa Denko, Toray Industries, NEC Corp., CNRI-Mitsui), Korea (ILJIN Nanotech, RIST), Canada (Raymor Industries Inc.), Cyprus (Rossetter Holdings Ltd.), Norway (n-TEC), Greece (Nanothinx). The World Market of carbon nanotubes now is in a stage of formation; its active action is predicted in 2–3 years [1].

In 2004 American Carbon Nanotechnologies had an installation for manufacturing carbon nano-materials (CNM) with productivity 4.5 kg/day, planning to increase the productivity up to 450 kg/day. In France CNRI produces CNM from 40 to 120 ton/year, Arkema – up to 5 ton/year; in China Shenzhen Nanotech – 10 ton/year, in Belgium – 5 ton/year. Norway is planning to produce up to 50 – 200 kg/day. Whole manufacture of CNM in 2004 was 65 ton, a total sum of sales was € 144 million, and in 2006 it reached $ 231 million. Annual growth exceeds 60 %. In 2010 the growth of sales has reached approximately

€ 3 billion (by other estimations up to 5 billion USD). The accelerated manufacturing output is observed in China and Korea. It is expected, that in the nearest future China will surpass the USA and Japan. The price of CNM constantly decreases being in the range 0.1 – 500 $/g; the instability of prices depends on morphology and purity of materials.

In Russia Tambov factory "Komsomol" together with the open company of scientific and technological center "Pomegranate" opened pilot production in 2007, manufacturing output being 200 g/hour. Market development of carbon nano-materials in Russia is tightly connected with the development of simple and inexpensive methods of their reception in laboratory conditions. Therefore there is necessity for development of reception methods as well as for methods of purity analysis of various fullerenes. In this paper we investigated the product purity of fullerene C-60, synthesized in different laboratories.

2. Leonhard Euler and fullerenes formation

In 1758 Leonhard Euler has proved the theorem that for any convex polyhedron the number of its faces (F), edges (E) and apices (A) is connected by the formula A–E+F =2. One of the consequences of this theorem bears on the structure of fullerenes [2]. It states that there is no convex polyhedron, all sides of which are hexagons. Therefore, a molecule C-60 and any other fullerene along with hexagons should have also pentagons. The latter are necessary for a curvature of a flat hexagonal graphite structure and its following transformation into a closed shape. For any such molecule F = p + h, where p and h is the number of pentagonal and hexagonal faces respectively. Each edge belongs to two, and each apex to three adjoining faces, so 6 (F–E+A) = p. From this equation together with Euler's equation it follows that p = 12.

Therefore in any fullerene the number of pentagonal faces is equal to 12. The number of hexagonal faces can be various, the number of apices always being even. Thus the least of possible fullerenes, C-20, consists of only 12 pentagons. The high stability of fullerenes is connected with high symmetry, and its symmetry is characteristic for fullerenes with isolated pentagons; the least of which is C-60, and following is C-70. With increase of carbon atoms the form of fullerenes deviates from a spherical one. Theoretically almost any carbon molecule or nanocluster consisting of penta, hexa, and heptagons has the right to existence. Therefore analyzing fullerene blends, this possibility must not be ruled out.

Comprehensions of fullerenes formation have undergone transformations. At first, it was supposed that fragments of carbon minelayers evaporated from a surface and then turn rolled up into a spherical molecule. Later it was shown that fullerene growth begun of carbon pairs. Ablation of carbon atoms by plasma action leads to the cluster growth in the form of linear chains which later create stable ring structures. There is also other models of fullerene synthesis [3].

3. Experimental procedure

The purity degree (a share of the basic product) as well as quantity and kind of an impurity are specified in a certificate. These data, as a rule, are obtained by the method of liquid chromatography. Liquid chromatography is the most effective method for analysis of organic complex structures which consists of two stages:

1. Separation of a test specimen into components;
2. Detecting and measurement of the contents of each component.

The separation is achieved by means of a chromatography column which is a tube filled by a sorbent. Carrying out the analysis, one passes through the chromatography column a certain liquid with a constant rate. Components of a test sample enter into the chromatography column and because of their different affinity to the sorbent, move with various rates and reach a detector at different times. Thus the chromatography column is responsible for

selectivity and efficiency of components separation. Selecting various types of columns it is possible to regulate a degree of separation of analyzed substances. Identification of compounds is carried out on the basis of their delay time. Quantitative measuring of each component is based on the value of a signal measured by means of a detector connected with the output of chromatography columns.

In our laboratory alongside with high efficiency liquid chromatography (HELC) we used also infrared radiometer and weight-spectrometer analysis. For interpretation of infrared absorption spectra of C-60 it is necessary to have information on its vibration spectrum. To calculate these characteristics, one usually uses quantum chemical methods, in particular, Hartree-Fock-Roothaan method [4]. The results of such calculation for C-60 give the following vibration frequencies for four lines 529, 567, 1275 and 1569 cm^{-1}. The action of a weight-spectrometer is based on space- time separation of ionized particles of investigated substance in a cross-section magnetic field. The ionic-optical system has double focusing of a bunch of ions. The researched substance is located into a Knudsen cell, then it is evaporated and is placed in an ionization chamber where is subjected by electronic impact. As a result, ions are formed in a bunch which passes through a weight analyzer. The bunch is analyzed with the help of magnetic field and a voltage analyzer.

4. Fullerenes purity and analysis of their blends
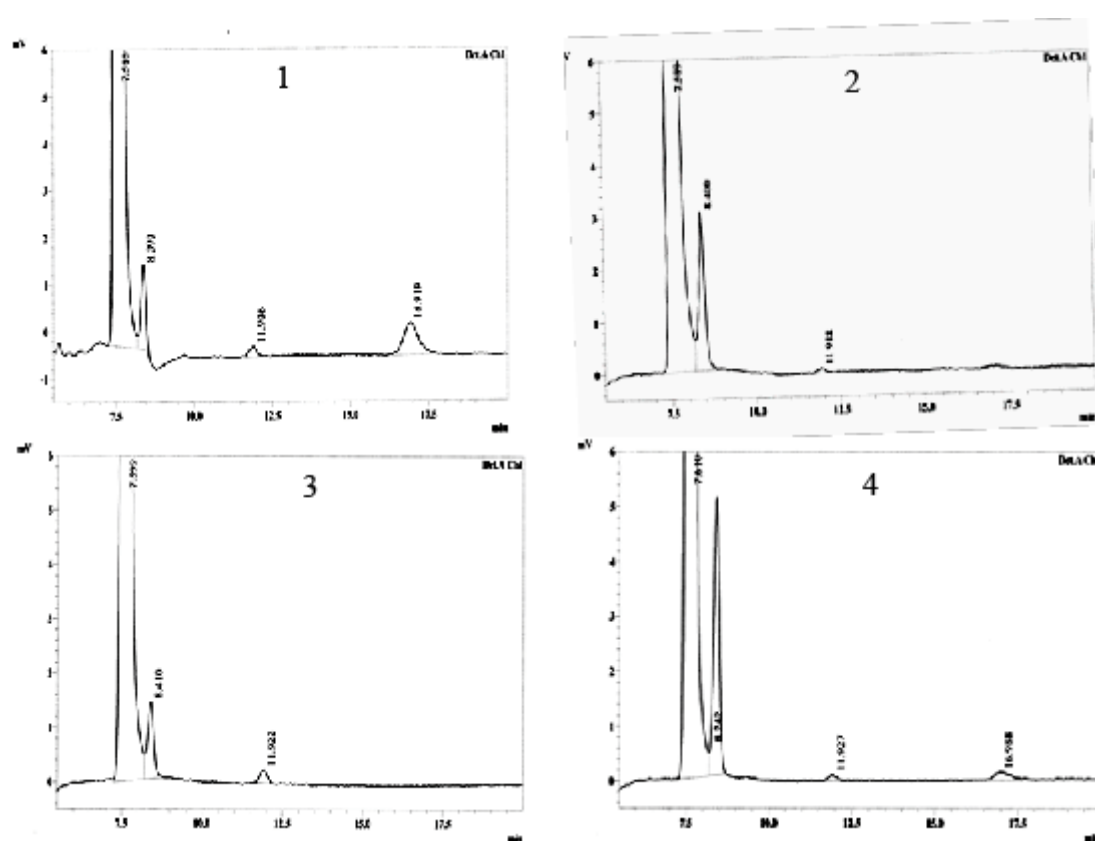The results of analysis are presented in Figs. 1–3.

Fig.1. Chromotograms of different samples.

The declared content of fullerene C-60 is in all four samples is 99.5 % (delay time 7.5 minutes). However, according to chromatography analysis (Fig. 1) sample 1 has 96.7 %

C-60, sample 2 – 98.9 %, sample 3 – 99.2 % and sample 4 – 97.7 %. In addition, it is found that from 0.02 up to 0.09 % C-70 (delay time is 12 minutes). Besides, samples 1 and 4 have C-60 dimers (delay time approximately 17 minutes). In all samples there is from 0.5 to 1.5 % of admixture (delay time 8.5 minutes). In literature it is imputed to C-60 fullerene oxide. However, we cannot establish it adequately.

Infrared absorption radiometry results are shown in Fig. 2. There are lines of 526, 576, 1182 and 1429 cm^{-1} which are close to the calculated lines 529, 567, 1275 and 1569 cm^{-1} indicating I_h symmetry. In addition, we observed the vibration frequencies at 1539, 2328 and 2360 cm^{-1}.
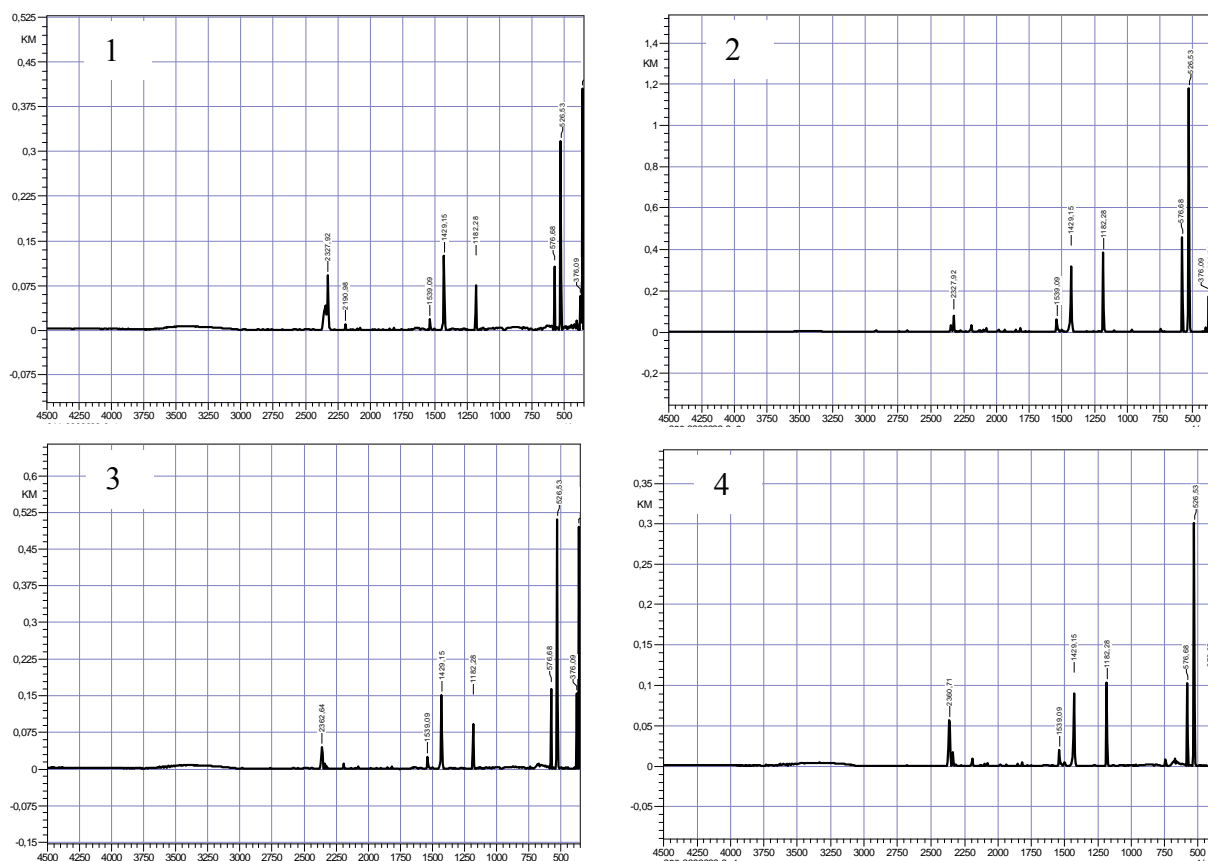

Fig. 2. Infrared radiometry of sample absorption.

Mass spectra are shown in Fig. 3. They indicate that in all samples the content of basic product C-60 is essentially less than it is given by chromatograms. In sample 1, it is 92.4 %, in sample – 94 %, in sample 3 – 92.7 % and in sample 4 – 93.4 %. We incline to explain this noticeable difference in all samples by the presence of mainly C-56 and C-58 fullerenes which chromatographically are not separated from C-60. To check this assumption on occurrence of C-56 and C-58 from C-60 during ionization in the mass spectrometer, we measured the mass spectra of C-60 derivatives with oxygen. The mass spectra corresponding to these molecules were obtained in a distinct manner. If ionization produces fragmentation of these molecules, we could be able to found out them. However, the energy of dissociation for fullerene–oxygen is ~ 240 kilojoule/gram-molecule, whereas that of into C-2 and C-58 is ~ 1500 kilojoule/gram-molecule. Therefore, the fragmentation C-60 fullerene due to ionization in mass spectrometers is highly improbable.
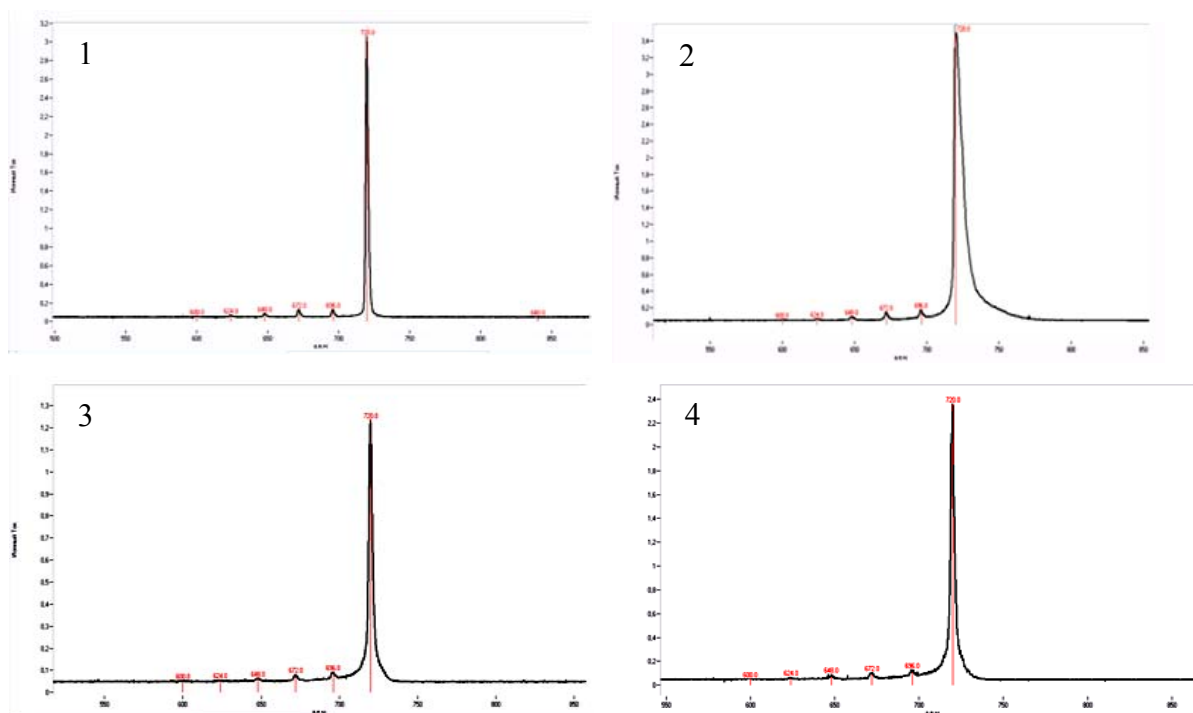
Fig.3. Mass spectra of samples.

5. Conclusion
Any considered method of purity analysis of C-60 fullerene taken individually does not allow determine an exact composition of samples. It is necessary to use in addition to traditional chromatography a method of mass spectrometry.

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