EXTRACTION OF FULLERENES FROM SHUNGITE CARBON BY WATER-CONTAINING SOLVENTS.

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INTRODUCTION

Detection of $\text{C}_{60}$-$\text{C}_{70}$ in the visible film within carbon-rich shungite (ShC) by electron microscopy and mass spectroscopy provoked a large number of experiments on extraction of native fullerenes from ShC. Numerous attempts of extraction by conventional methods were not always successful. The latter supposed to be caused not only by heterogeneity of occurrence of fullerenes in ShC but mostly by the way of interaction of fullerenes inside carbon matrix. Thus occurrence of fullerenes in ShC is still questionable. Nevertheless ShC is always remembered in connection with the problem of concentration and preserving of fullerenes and nanostructures in nature.

Recent achievements of generation of water soluble fullerenes (FWS) prompt to revision of the approach to extraction of fullerenes from ShC. The difficulties in extraction were supposed to be connected with interaction of fullerenes in ShC by donor-acceptor bonds rather than hydrophobic ones which were considered before. The present study was undertaken to check this supposition.

EXPERIMENTAL

Method worked out for FWS was tailored for extraction of fullerenes from ShC. The stable water colloidal solutions of fullerenes (in the form of hydrated clusters 3-36 nm in size) were used as a standard in this study. Powdered ShC (from Shunga deposit) was subjected to ultrasonic treatment in water with addition of toluene-alcohol (4:1 v/v) until complete evaporation of toluene phase. Then mixture was filtered and centrifuged at $4 \times 10^3$ g. Stable gray-brownish and opalescent in reflected light solution was obtained.

Mass spectrometric measurements were carried out using time-of-flight MSBC mass spectrometer (“Selmi”, Sumy, Ukraine) by the $^{252}$Cf PID method. UV-VIS spectra of colloidal solutions and IR-spectra of powdered dry films dispersed homogeneously in KBr pellets, were performed respectively by spectrometers "Specord M-40", "Specord M-80", Germany.

RESULTS AND DISCUSSION

Mass-spectrum of positive ions of the water colloidal solution of ShC re-dissolved in hexane showed prominent peaks with m/z 720,66 a.e.m, correspondent to signal of C$_{60}$ molecular ion (Fig.1). UV spectra of water solution demonstrated wide band at $\lambda_{\text{max}}$ 265-267 nm. Adsorption
UV-spectra of the solution dried under vacuum and re-dissolved in hexane had intensive bands at $\lambda_{\text{max}}$ 213, 256, 330 nm. Evaporation of the solution under air brought to the formation of a blackish film insoluble in water and organic solvents. IR-spectra of the film contained wide bands attributed to the C$_{60}$ and its derivatives at 576, 1183 and 1430 cm$^{-1}$. Thus formation of insoluble films could be caused by polymerization of colloidal particles contained fullerenes.

Fig. 252 Cf desorption mass spectrum of re-dissolved in hexane water-soluble extractions from ShC

Concentration of fullerenes extracted by the method described was c.a 10$^{-3}$%. The data were repeated on several batches of ShC samples. That allows us to concentrate extracted from ShC fullerenes, their derivatives and nanostructures for further investigations.

Comparative analyses of extracts obtained from ShC and C$_{60}$FWS (a donor-acceptor complexes of fullerenes and water) lead to a supposition that fullerenes in ShC are presented mainly in the form of chemical derivatives and strong molecular complexes, which are likely to be stabilized by means of donor-accepted interactions than hydrophobic ones. In fact, destruction of such donor-acceptor complexes had to be easier in polar solvents than in non-polar ones (toluene, hexane). The fact was confirmed during this study.

**CONCLUSIONS**

- Method worked out for production of FWS was applied to extraction of fullerenes and nanostructures from ShC
- Molecular complexes of fullerenes with polar molecules and oxygen contained fullerene derivatives were identified in ShC aqueous solution. Native fullerenes and some of its derivatives could be extracted by non-polar solvents only after water evaporating.
- Polymeric film insoluble both in water and in organic solvents is formed while evaporating of ShC water colloidal solution under air.

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**REFERENCES**
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