EVALUATION OF SOLID STATE METHODS TO DETECT FULLERENES IN GEOLOGICAL MATERIALS

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INTRODUCTION

Since the discovery of fullerenes [1], C_{60} has been detected in various geological materials in trace concentration, usually not exceeding 10 ppm. These include hard solid bitumen from Shunga, Karelia, Russia [2], and Mítov, Bohemian Massif [3], impact breccia from the Sudbury impact structure, Ontario, Canada [4, 5] , fulgurite from the Sheep Mountain, Colorado [6], clays from the Cretaceous-Tertiary boundary [7] and rocks from the Permian-Triassic boundary [8]. However, many of these results have been discussed, frequently in terms of the analytical methods used for detection of fullerenes [9, 10]. Analytical methods used in previous works comprise high-preformance liquid chromatography of previously solvent (toluene, CS_2 etc.) extracted material by stirring, ulrasonication or Soxhlet. Further, mass spectrometry is commonly used with different ionization sources (EI, LD). In addition, several methods have been used in some occasions, e.g. Raman microspectrometry [11] or high-resolution transmission electron microscopy [2]. Aim of our work was to compare analytical methods, which do not require previous solvent extraction, i.e. they are applicable directly to the ground geological sample. We used prepared mixtures of C_{60} with different geological matrices in various concentrations and subjected them to high-resolution transmission electron microscopy (HRTEM), Raman microspectrometry, and time-of-flight mass spectrometry with laser desorption (LD-TOF-MS).

EXPERIMENTAL

Hard solid bitumen from Shunga, Karelia, graphite from Český Krumlov, bituminous coal from Kladno, both Bohemian Massif, as material with different carbon content and structure and quartz as reference inert material were used for our experiments. All were ground in agate ball mills and sieved through 500 μm mesh to obtain powders with comparable grain size. Such prepared matrices were then impregnated with toluene solution of pure standard C_{60} and unseparated mixture of fullerenes containing C_{60} , C_{70}, C_{78} and C_{84} (both provided by Xillion, Germany). The mixtures were left at room

temperature in dark to evaporate substantial part of toluene but no special action was made to remove all solvent from the samples because of danger of potential destruction of fullerenes. Then, the mixtures were gently mixed in agate mortar. Resulting concentrations of C_{60} in solid samples varied from 1 to 900 ppm. Another series of samples was made by dispersing previously weighed solid C_{60} directly in the powdered geological materials. Resulting concentration of C_{60} was approximately 1%. For HRTEM observations, Phillips CM-20 was used in lattice fringes and selected area electron diffraction modes. For Raman microspectrometry measurements spectra were recorded with a Dilor confocal microRaman spectrometer equipped with a cryogenic Wright Model CCD 05-11-0-202 chargecoupled detector (CCD). The excitation source was the 514.5 nm of a Coherent Innova Model 90-5 Ar+ laser operating at approximately ten milliwatts on the sample. Integration times ranged from 60 to 300s. TOF spectra were taken on TofSpec 2E (Micromass, UK) spectrometer running in linear mode, with positive ions. Operating voltage was 20kV, pulse voltage 1.8 kV. N_2 laser was used for the ionisation with 50% laser course and 50 laser fine. Sample was dispersed in small amount of toluene to make slurry, no matrix was used in this case.

RESULTS AND DISCUSSION

Although HRTEM has provided valuable information about the state of dispersion of fullerenes in the geological matrix, its quantitative sensitivity did not exceed 100 ppm of C_{60} concentration. C_{60} was observed mostly as aggregates of nanocrystals with diffraction patterns typical for hexagonal close-packed structure (hcp). C_{60} tends to crystallise in this symmetry when impurities, such as other fullerenes or residual solvent are present [12]. For experimental mixtures with solid C_{60}, patterns for hcp, as well as for fcc (face-centered cubic) structure were observed. Similar observations could have been made on samples with added fullerene mixture, with diffraction pattern of all aggregates typical for hcp. With C_{60} concentration in the sample bellow 100 ppm, we were not able to observe any particles containing fullerenes. Either the fullerene aggregates were not sufficiently large or their number was just so small that we could not find them.

According to group theory, single C_{60} molecule has only 10 Raman-active frequencies due to its high icosahedral symmetry. At room temperature the most intensive A_g (tangential breathing mode) band appears at 1459-1469 cm^{-1} [13]. The precise position of this bands is influenced by the presence of oxygen in the structure of fullerites [13]. Nevertheless, when comparing with the graphitic G band at 1580 cm^{-1} and D band at 1350 cm^{-1}, the F band is very distinctive. Unfortunately, the presence of surrounding carbonaceous matter in the sample may arise some methodological problems, especially considering the laser power. Due to partial absorption of the laser light by black carbonaceous matter, temperature was increasing, which caused observable destruction and subsequent loss of signal at 1460 cm^{-1}. Therefore the laser power had to be reduced even more and the laser beam defocused. Resulting sensitivity for detecting C_{60} in the matrix was 100 ppm. Different instrumental setup is now being tested for better detection of fullerenes.

Amongst tested methods, LD-TOF-MS was determined as the most sensitive, especially when detecting C_{60} in matrices with low content of volatile carbonaceous compounds. For bituminous coal, which contains the most of those comparing to shungite, graphite and quartz, we were able to unambiguously detect C_{60} at concentration of 10 ppm, at lower concentrations, the peak at m/z 720.6 was hidden in the surrounding noise. For shungite and graphite, the limit was 1 ppm, but the signal was already hardly distinguishable from the surrounding matrix. Reliability of such spectra cannot be taken as very high and obtained results must be handled with maximal care. Fig. 1 shows LD-TOF-MS spectra in the range *m/z* 680-790 of pure and spiked shungite with 1 and 10 ppm C_{60}.
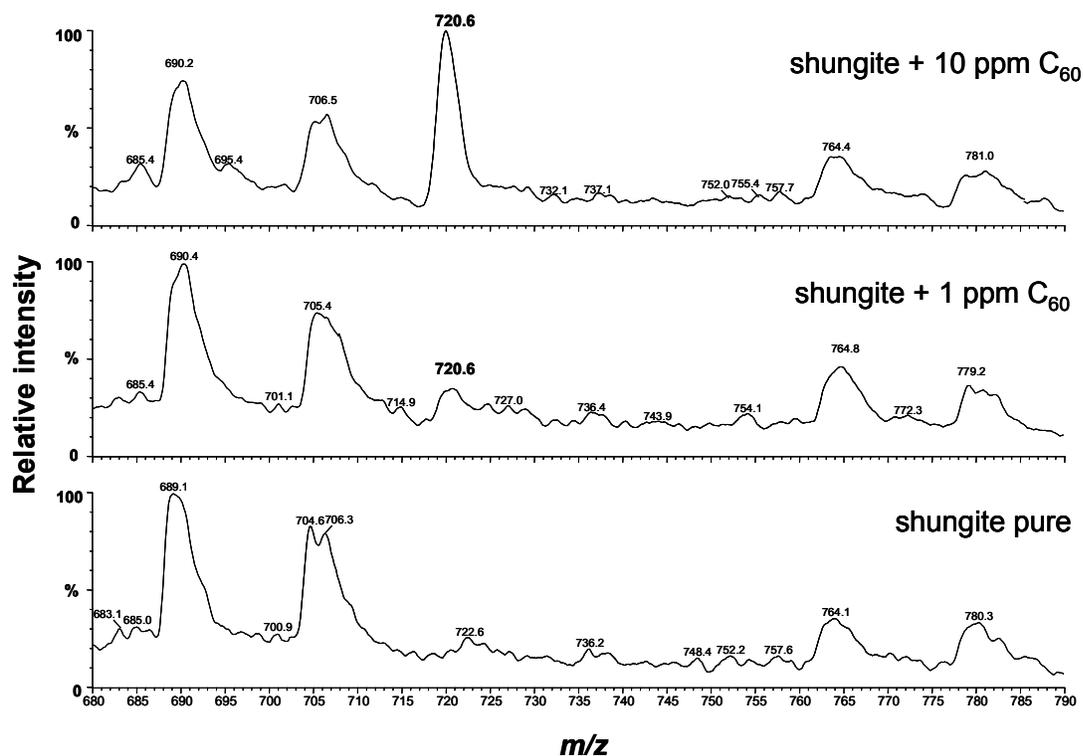

Fig. 1. LD-TOF-MS spectra of pure shungite (bellow), spiked with 1 ppm C_{60} (middle), spiked with 10 ppm C_{60} (top), *m/z* range of 680 to 790 obtained in linear mode, the mass reported represent average MW.

CONCLUSIONS

Different solid-state methods (high resolution transmission electron microscopy, Raman microspectrometry, and LD-TOF-MS) were used to investigate their sensitivity for the detection of fullerenes in different natural carbonaceous matrices (hard solid bitumen, graphite and bituminous coal) and quartz. The most sensitive is the mass spectrometry with the detection limits of 1 ppm for graphite and shungite and 10 ppm for coal. Raman microspectrometry could be a promising tool for investigation of the state of fullerene

dispersion in the matrix, but great attention has to be paid to the instrumental setup, and until now it has not been possible to determine fullerenes in contents lower than 100 ppm in the carbonaceous matrices. HRTEM is amongst these the only technique that allows direct imaging of the fullerene crystallites in the matrix but looking for C_{60} in low concentration is very difficult.Moreover, randomly dispersed fullerenes spheres, without packing along a crystalline order, are quite impossible to detect by HRTEM. As conclusion it can be said that only the mass spectroscopy can be used to search for fullerenes in solid geological samples but a great care has to be taken when evaluating such obtained results.

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