Identification of Carbon Nanostructures (Fullerenes) in Cigarette Ash

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Abstract:

The production of fullerene materials (C_{60}, C_{70}, etc.) has recently become a matter of increasing commercial interest and environmental concern. Although fullerene toxicity remains poorly defined, some forms have been shown to have cytotoxic effects, particularly when exposed to microbial communities. Therefore, the identification of (potential) fullerene sources is an important first step towards an accurate environmental exposure assessment. In this work, we tested the hypothesis that fullerenes (as C_{60} and C_{70}) are formed in burning cigarettes by analyzing ash from several scenarios, including mimicked smoking events.

Introduction:

Since the discovery of fullerene in 1985 by Kroto, et al., many synthetic methods have been proposed. Of particular interest is the synthesis of fullerene via pyrolysis of naphthalene [1]. This low molecular weight polycyclic aromatic hydrocarbon (PAH) can be found in environmentally significant quantities in coal tar, hydrocarbon fuels, and cigarette smoke [2, 3]. Pyrolysis has often been shown to occur in oxygen deficient environments inside a burning cigarette. Temperatures typically range between 700 and 920°C, but occasional microenvironments can reach up to 1200°C [4]. Previous studies have found the formation of fullerene via pyrolysis of PAHs to occur in the 1000-1100°C range [1, 5]. In this work, we demonstrate fullerene production via pyrolysis of high-tar cigarette tobacco.

Concern over the potential environmental impact of fullerenes has risen sharply in recent years. Although pristine C_{60} has been considered to show minimal cytotoxicity to rat lungs and microbial communities, functionalized C_{60} has been found to show some level of cytotoxic effects [6, 7]. Fullerene water suspensions have been demonstrated to show pronounced cytotoxic effects when exposed to *E. coli*, *P. aeruginosa*, and *B. subtilis* [8, 9]. Additionally, fullerene exposure to ozone can also result in increased levels of toxicity. Ozone will add to a fullerene 6,6-double bond to form a 1,2,3-trioxolane which spontaneously converts to the fullerene epoxide, $C_{60}O$, producing singlet oxygen, a reactive oxygen species known for lipid peroxidation and membrane degradation [10]. Thus, inhalation of fullerene and exposure to even minimal amounts of ozone could lead to compromised membrane integrity in human lungs.

Therefore, considering the potential environmental impacts of C_{60}, our study sought to shed light on a (potentially) prevalent but previously unknown source of fullerenes.

Experimental Procedure:

Six samples of domestic cigarette tobacco and a control of untreated whole leaf Burley tobacco were pyrolyzed at various temperature maximums over a range of pressure profiles using a Thermcraft Protégé split tube furnace. Trials were performed under 100% argon flow with linear flow rates between 0.242 and 2.55 liters per minute. Smoke particulates were collected using PTFE 0.2 μm particulate filters and soluble ash and particulates were extracted into toluene using a Soxhlet apparatus. Two ash samples were also produced using custom-made smoking machines and extracted using the Soxhlet apparatus. Analysis on all samples was performed using a MALDI-TOF mass spectrometer.

Results and Conclusions:

MALDI-TOF analysis is believed to indicate fullerene content in the majority of ash samples. Seven of the nine samples displayed a possible C_{60} m/z (mass-to-charge ratio) peak of 720 and/or C_{70} m/z peak of 840. The remaining two samples displayed peaks that could correspond to hydroxyl and epoxy group additions to C_{60} or C_{70}. Of particular interest was evidence of C_{70}, but no clear amount of C_{60}, in M1, a sample run under high pressure and temperature. The most abundant amount of C_{60} appeared in M100-8, a sample run at lower temperature under near atmospheric pressure. Sample conditions are shown in Table 1. Overall, the spectral data provided compelling evidence for the formation of the C_{60} and C_{70} fullerenes during cigarette smoking events.

Based upon these results, we make the following recommendations to the scientific community: 1) Cigarettes should be viewed as potential sources of fullerene environmental exposure, 2) Increased effort should be given to proper cigarette containment and ash disposal until the environmental effects of fullerenes are more fully understood, 3) Further research should be conducted in this area. Ultimately, the evidence shown in this work should be used to promote healthier and safer environmental conditions.

Future Work:

Further analysis is needed to confirm the presence of C_{60} and C_{70} in current samples. High performance liquid chromatography (HPLC) could be used to verify molecular UV-Vis spectra and retention times. In the future, additional high-carbon pyrolysis events should be investigated as potential fullerene sources. Cigar smoking is a natural candidate for such studies, as are forest fires and lean hydrocarbon fuel combustion.

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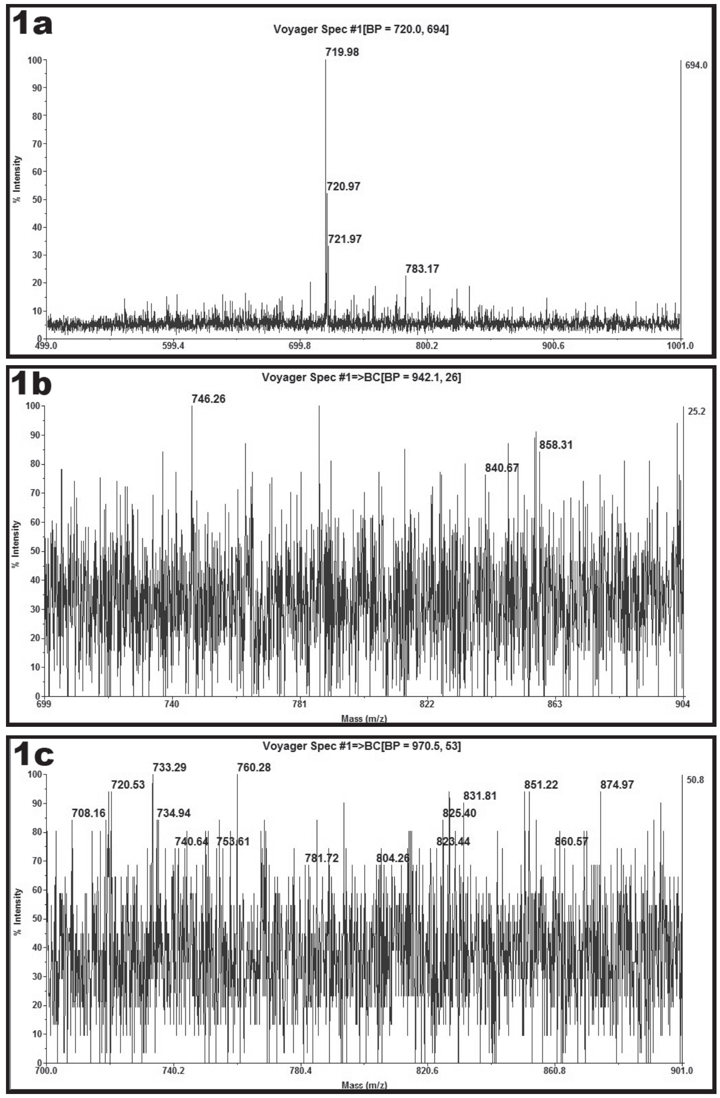

Figure 1: MALDI-TOF mass spectrum of samples a) M100-8, b) M1, and c) SM.

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Sample ID	Temperature Set-point (°C)	Initial Tube Pressure (torr)	Result
M1	1200	~2100 (~40psi)	Possible C70
M5	1200	608	C60
C6	1200	622	C60
M7	1200	747	Possible C70
M100-8	800	735	Large C60
C9	800	684	C60
Control	800	487	No Fullerene
SM*	Natural	Natural	No Fullerene
SC*	Natural	Natural	C60

Table 1: Summary of sample conditions and results.