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## **Nanoparticles in the time of flight mass spectrometer**

## Nanoparticles in the Time-of-Flight Mass Spectrometer

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### Abstract

The time-of-flight mass spectrometer (TOF-MS) is discussed for the analysis of nanoparticles. It can be used online for a variety of nanoparticle systems. In particular, the application of the TOF-MS for the study of combustion aerosols is considered. Results are shown for species taken from laminar diffusion flames of methane and propane. The analyzed species are polycyclic aromatic hydrocarbons (PAH), fullerenes and soot particles.

Nanoparticles can be found in nature in various environments and can be produced in the laboratory. Their physical and chemical properties may vary remarkably from those of the corresponding bulk materials. For example, while the color of bulk gold is yellow, nanoparticles of gold are red. Particles of small size may be insulators while the bulk materials are metals. Also, the optical properties may be significantly different. Most of the changes happen when the size is reduced towards the nanometer range. Quantum confinement as well as surface effects have important influences on the particle behavior at this size. Electrons and quasiparticles, confined to a nanoparticle, occupy discrete energy levels and their locations depend on the size of the particles. In particular, the energy band gap can change dramatically with particle size. This can lead to a size-dependent metal-insulator transition.

It is apparent that the size determination of nanoparticles is an important issue if their properties are strongly related to size. In the 1970's nanoparticles were mostly analyzed using electron microscopy. This worked very well for the larger particles but it failed for the very small ones with diameters less than about 3 nm. Also, the particles had to be supported on a substrate, and carbon-coated grids had to be used for this purpose. In addition, particles from some materials had to be covered with a few carbon atom layers in order to become imaged. The size analysis by electron microscopy does not allow online-studies where the parameters of an experiment are changed and one can obtain the result immediately. Such fast information however is often important in particular when the growth process of nanoparticles is investigated. Online-size-analysis also allows building instrumentation based on feedback design, which enhances tremendously the efficiency of an experiment or industrial process.

The first time-of-flight mass spectrometer for clusters and nanoparticles was built in 1980<sup>1</sup>. It was used for the investigation of various growth techniques and for studies of

cluster stabilities. It soon was also built by other research groups in laboratories around the world and became the major instrument for studies of atomic clusters. By using a TOF spectrometer the clusters can be analyzed in beams at high vacuum conditions and their purity can be checked atom by atom. This led to precise procedures for gaining knowledge about physical and chemical properties of the particles. The discovery of fullerenes is just one of many outstanding findings about clusters and nanoparticles.

The first commercial TOF spectrometer became available about 15 years ago. In H. C. Siegmann's laboratory we started around 1990 to use such a TOF-MS for the research of combustion aerosols. The instrument has a very wide mass detection range, from single atoms to large molecules and to nanoparticles. The size range, which is covered, lies below the range accessible with traditional aerosol techniques like differential mobility analyzers (DMA). The DMA can be used down to particle diameters of about 3 nm<sup>2,3</sup>. However, there is no aerosol detection instrument for the smaller sizes. Yet, it is expected and also found, that the major changes in particle properties occur for particles smaller than 3 nm. Therefore, from the perspective of materials science, a detector for 3 nm and smaller particles is a fundamental requirement. Only in this size range the major changes, due to the quantum size effect and the enhanced surface-to-bulk ratio become dominant. The particles need to be analyzed atom by atom in order to study phase transitions, which may happen suddenly at a particular size.

Recently the TOF-MS received new attention a number of aerosol research groups. Online single particle analysis is now used for various purposes. In particular, laser induced evaporation of nanoparticles<sup>4</sup> became a promising technique used to study their chemical composition. Atomic and molecular species, which are vaporized from the particles, are analyzed in the TOF-MS and this is a procedure, which is fast and very accurate. One needs only very low particle densities, as the instrument is equipped with a single particle detector. It allows studying traces of an aerosol, which could not be detected by chemical methods. The TOF-MS can now be applied in basically every area of aerosol research, where small amounts need to be analyzed.

We have used the TOF-MS for the last 10 years to study the species in laminar diffusion flames. There are three types of species in such flames: organic molecules, fullerenes, and carbon soot particles. All three types can be analyzed with the same instrument. The species are extracted from the flame, diluted with nitrogen, and then transferred into the TOF-MS by a pulsed valve. There a molecular beam is formed by using a skimmer and differential pumping. The particle beam is cooled by supersonic expansion. The neutral beam is then crossed by the pulsed light beams of an excimer laser, which leads to positive ionization of the molecules and particles. A pulsed ion optics then extracts the ions and accelerates them into the drift tube of the spectrometer. After passing a reflectron to enhance the mass resolution the particles are analyzed using a channel plate detector. The detailed apparatus is described elsewhere<sup>5</sup>.

Fig. 1 shows a mass spectrum of polycyclic aromatic hydrocarbons (PAH) extracted for a laminar methane flame. We have analyzed PAH up to about 1000 amu. The results allow us to study the soot formation in its first stage when the primary particles are formed. The PAH are often considered as the precursors for soot formation and are therefore important to understand for this process<sup>6-10</sup>. However our detailed studies suggest that there is not the usually assumed relationship between PAH and soot.

The formation of soot particles rather happens simultaneously with the formation of PAH. Also, the successive-type growth of ever larger PAH has a side path, which occurs by coagulation reactions of PAH<sup>11</sup>. Such important information about the early stages of molecule and carbon particle formation is obtained by height profile measurements where the species are probed along the vertical center line of the flame<sup>5,12,13</sup>. Another important analysis is the intensity distribution of the peaks in the mass spectra. There are groups of peaks, which tell us about the relevant growth mechanisms<sup>14</sup>. For example, we have identified the bay closure mechanism for the successive growth. We find that bays in PAH can be either closed by acetylene, by benzene or by PAH<sup>15</sup>.

At high laser power and in an area just below the burnout region a broad band of mass peaks appear in the TOF spectra. This is shown in Fig. 2 for a propane flame. The mass peaks are due to pure carbon particles without any hydrogen content. The spectrum of Figure 2 gives the peaks over a wide mass range. The spectrum has the typical characteristics of a mass spectrum of fullerenes, which is the outstanding intensity of C<sub>60</sub>, and also of C<sub>50</sub> and C<sub>70</sub>. In addition, the peaks are at C<sub>2n</sub>, i.e. with a mass separation of 24 amu. Fullerenes can only occur with this mass difference, a condition given by the 5/6 network of the fullerene cage structure. This condition allows very clearly to identify fullerene peaks from soot particle peaks. The spectrum in Figure 2 extends to about 3000 amu, which corresponds to about 250 carbon atoms per particle. All mass peaks are well resolved. This is seen even better in the spectrum of Figure 3, which is taken in a smaller mass range, between C<sub>68</sub> and C<sub>116</sub>. The peaks are narrow and well separated. All peaks belong to the C<sub>2n</sub> series and are due to fullerenes. The antimagic number 72 are clearly seen as an intensity drop from the highly stable C<sub>70</sub> cluster.

In Figure 4 the transition region from PAH to fullerenes for a propane flame is shown. While PAH peaks decrease with size and become quite small above about 700 amu, the fullerene peaks increase, have a maximum at around C<sub>60</sub> and then decrease slowly with increasing mass. The superposition of peaks from PAH and fullerenes between 500 and 800 amu leads to an apparent background in the mass spectrum as it reduces the mass resolution in this area. However, as the peaks of PAH and fullerenes dominate in different mass ranges, the ability of the TOF-MS to simultaneously detect hydrocarbon and pure-carbon (soot) particles is well demonstrated.

Figure 5 shows the transition from PAH to fullerenes for a methane flame. Again, PAH peaks become small where the fullerene peaks start to emerge. A narrower mass range for this spectrum is shown in Fig. 6. The outstanding stability of C<sub>60</sub> is seen in the high intensity of this peak and also in the very low intensity of the C<sub>62</sub> peak. An antimagic number cluster (like C<sub>62</sub>) typically follows a magic number cluster (like C<sub>60</sub> in this case). C<sub>70</sub> is another outstanding peak with a following minimum at C<sub>72</sub>. The spectrum thus gives important stability information about the particles.

In the higher mass range one finds soot particle peaks with 12 amu distance. These particles do not have fullerene structure but rather are graphitic-like. Their atomic arrangement is considered to be honeycomb in small areas but disordered over larger dimensions. In Fig. 7 both fullerenes and soot particles are displayed. The fullerene peaks become small at around 2000 – 3000 amu and then, at higher masses, the soot particles are detected. The intensity of their distribution is relatively small but one needs to

consider that a big particle contains a large number of carbon atoms and therefore the amount a carbon per mass range is high.

Fig. 8 shows the same transition region from fullerenes to soot particles. Soot particles up to 7000 amu are detected. The largest mass corresponds to carbon particles with about 600 carbon atoms. These large soot particles are detected simultaneously with the fullerenes.

In conclusion, we have used a TOF-MS with pulsed laser ionization to study aerosol particles from laminar diffusion flames. Three types of species are identified: PAH, fullerenes, and soot particles. The PAH analysis gives important information about their growth processes. The analysis of fullerenes and soot particles can be related to the PAH profiles which allows to obtain a new view of the chemical processes which govern the formation of hydrocarbon and all-carbon molecules. Such studies help to identify the soot forming chemistry, in particular the onset of this growth where the primary particles are formed. The relationship between the growth of the species, i.e. the PAH, the fullerenes and the soot particles is important for their control in the flame. If one wants to use flames for the production of fullerenes, the initial conditions for their formation could be improved after such TOF-MS studies. If one wants to suppress the soot formation, the growth of the primary particles and their relationship to the PAH growth has to be known<sup>16,17</sup>. The simultaneous detection of the three types of species in the TOF-MS and the measurement of their height profile helps to identify the chemical pathways in the different parts of the flame. Such studies are important for material science, aerosol research, and nanoparticle and cluster studies.

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\* The work has been done together with K. Siegmann at ETH Zurich.

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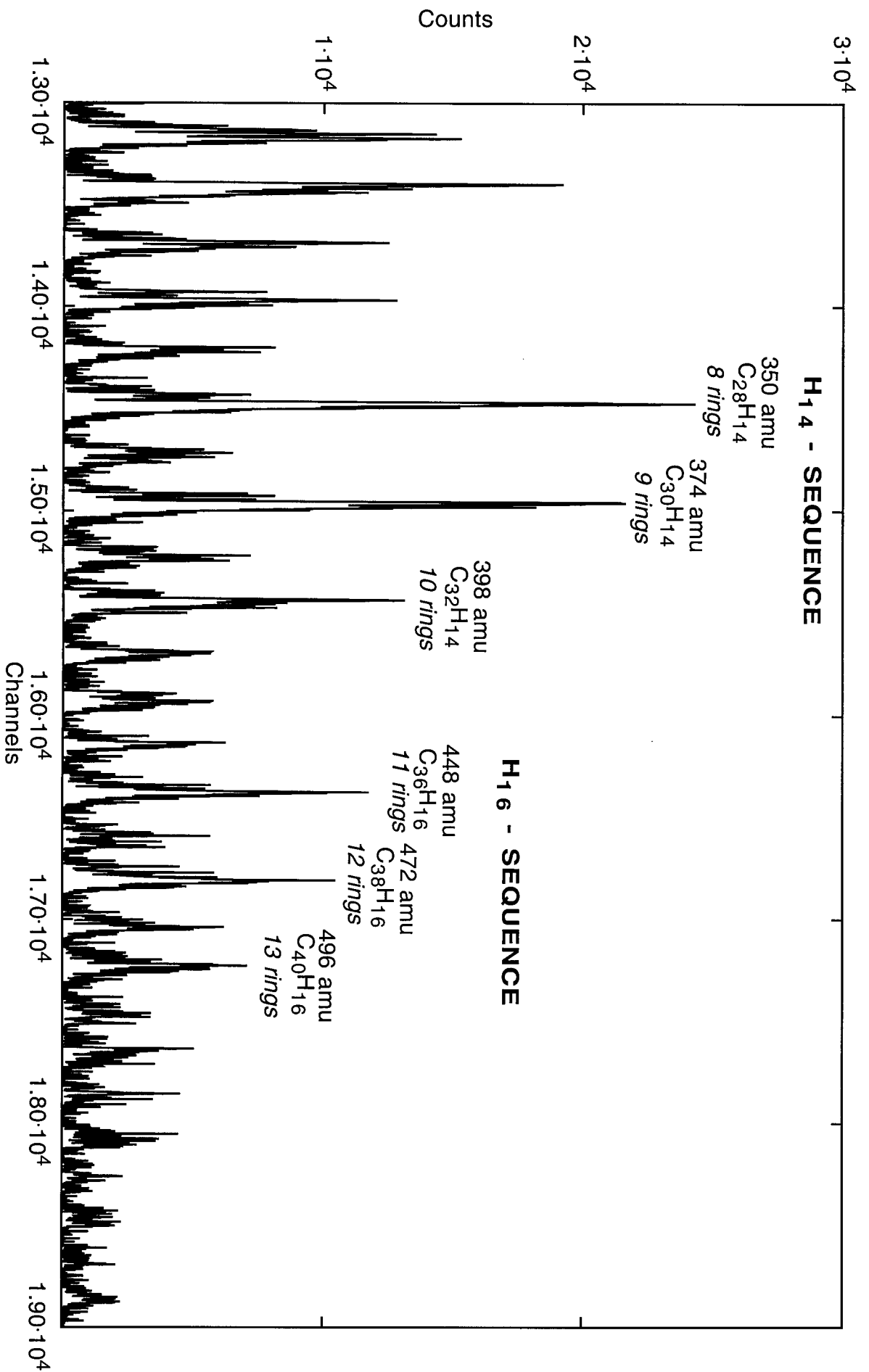


Fig. 1. Time-of-flight mass spectrum of polycyclic aromatic hydrocarbons (PAH) extracted from a methane diffusion flame.

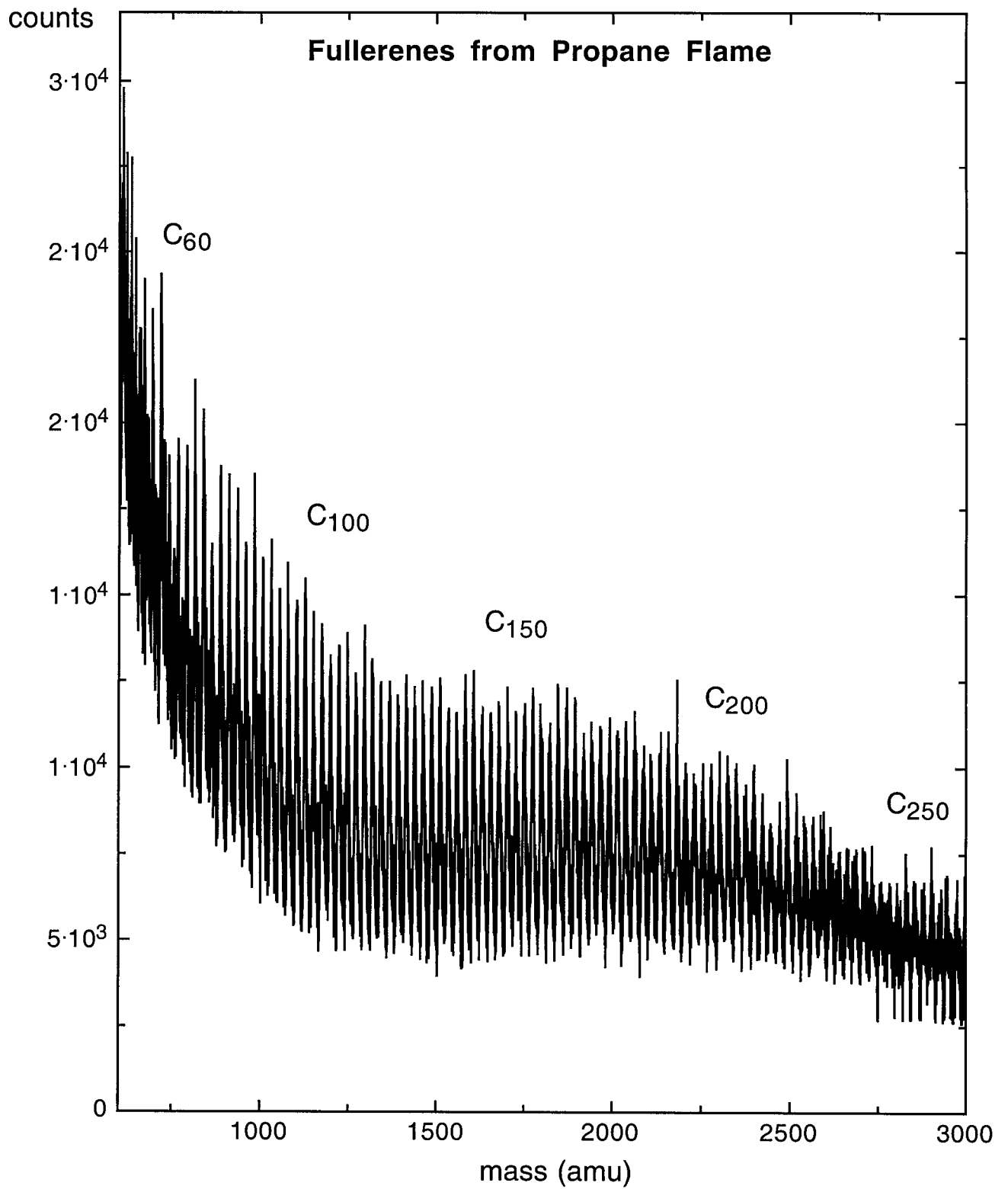


Fig. 2. Fullerene mass spectrum, taken from a propane flame.



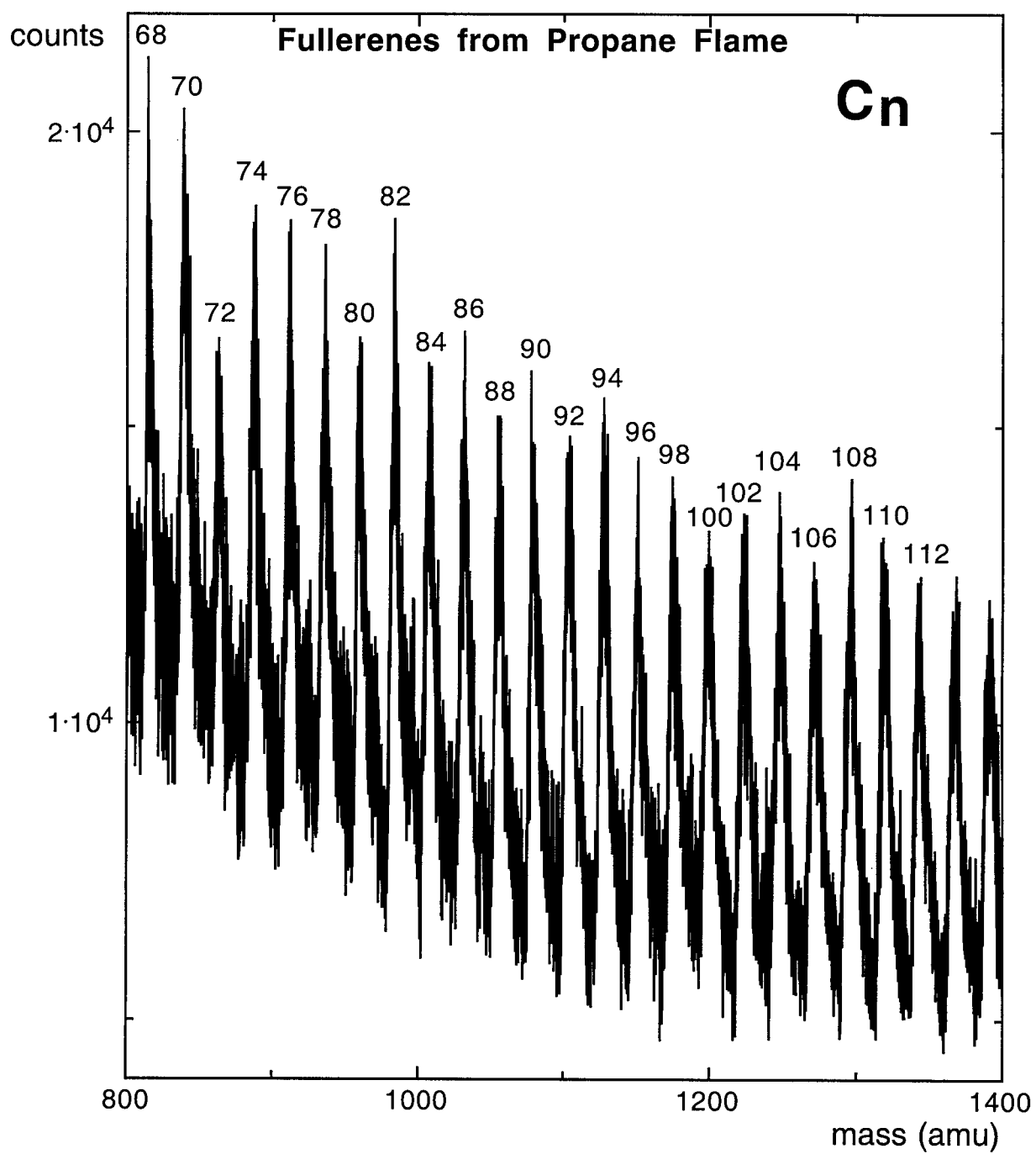


Fig. 3. Section of a mass spectrum of fullerenes from a propane flame.

# PAH's and Fullerenes from Propane Flame

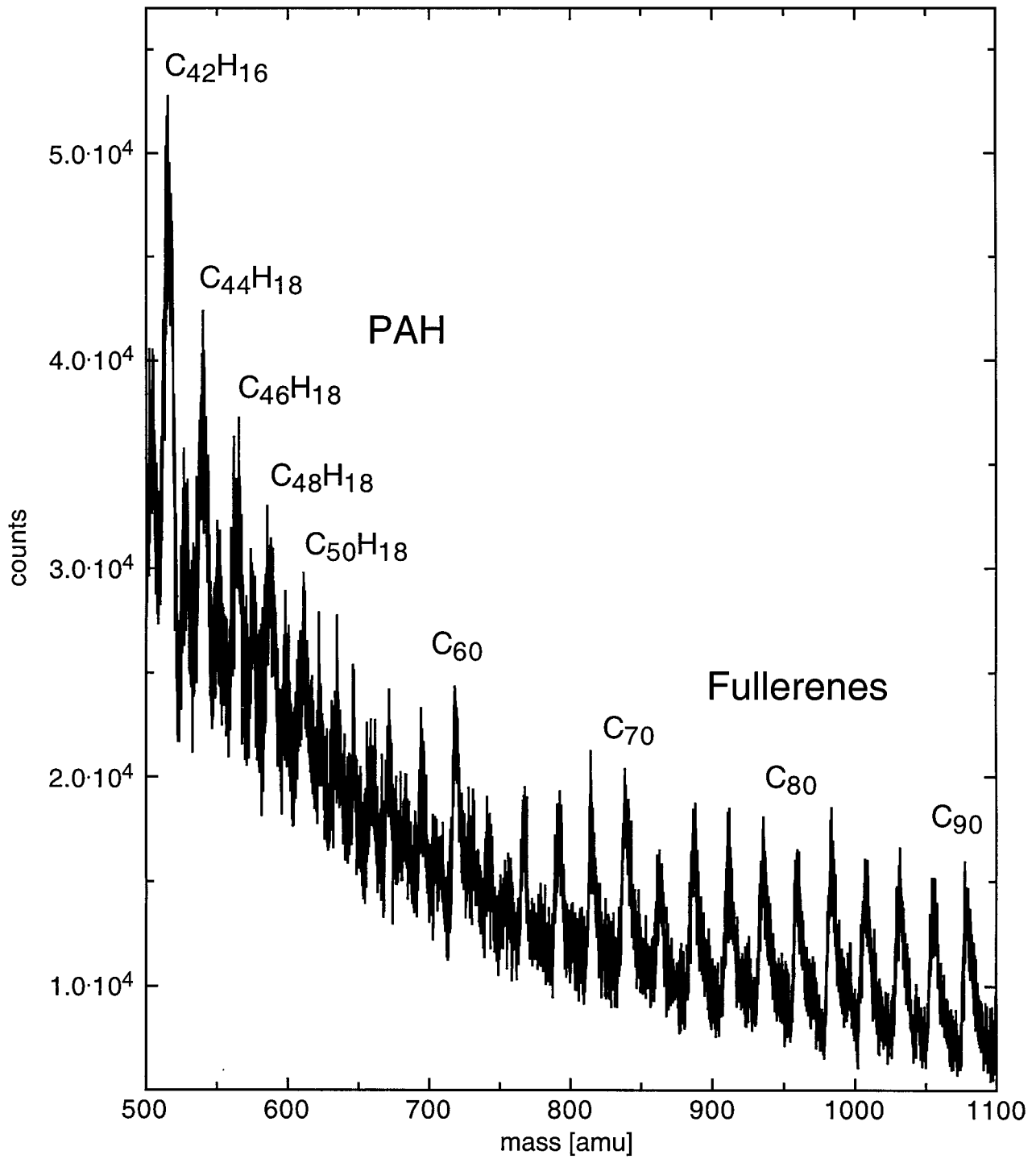


Fig. 4. Transition region between PAH and fullerene mass peaks.

# PAH's and Fullerenes in Methane Flame

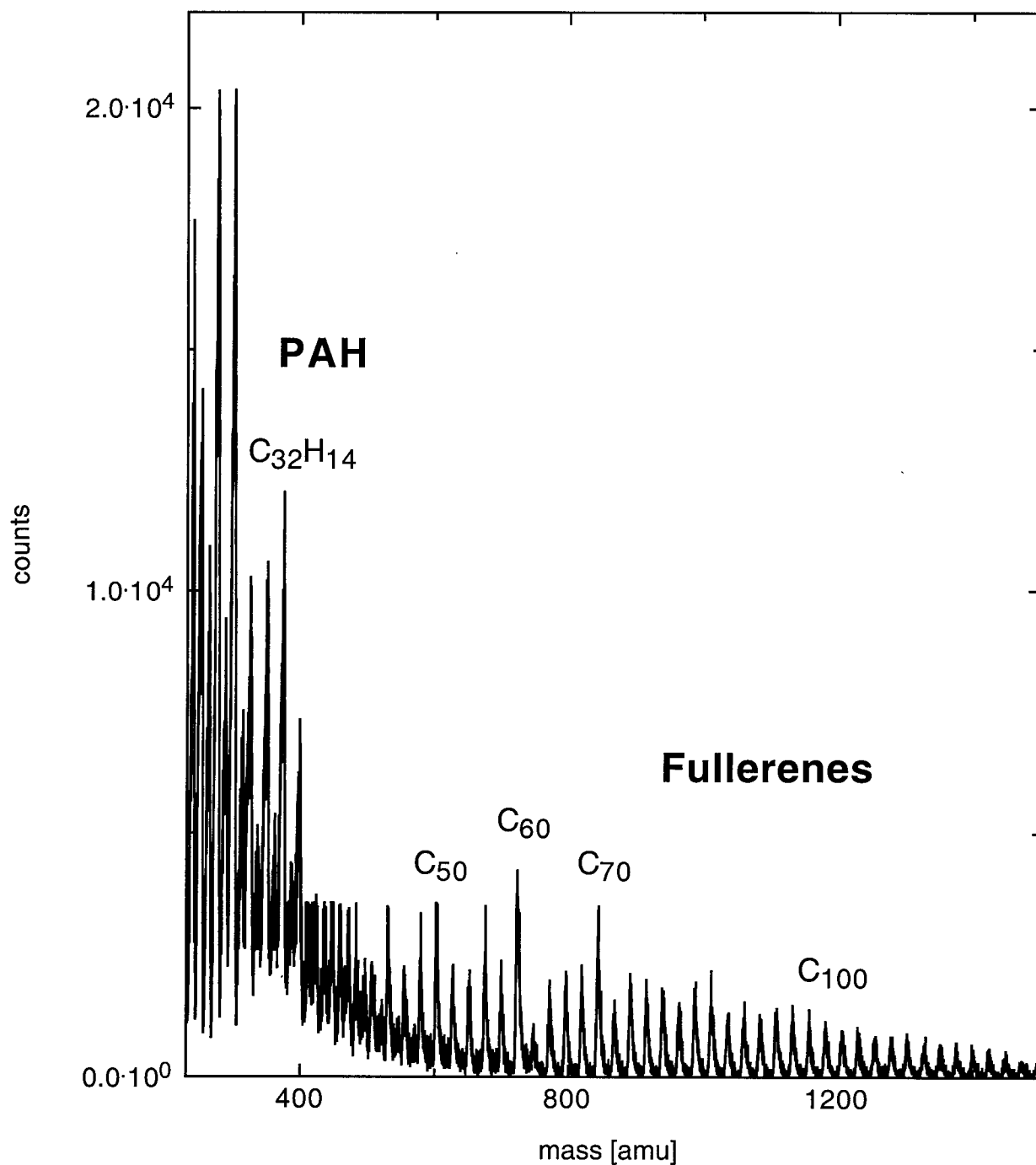


Fig. 5. PAH's and fullerenes extracted from a methane flame.

# Fullerenes in Methane Flame

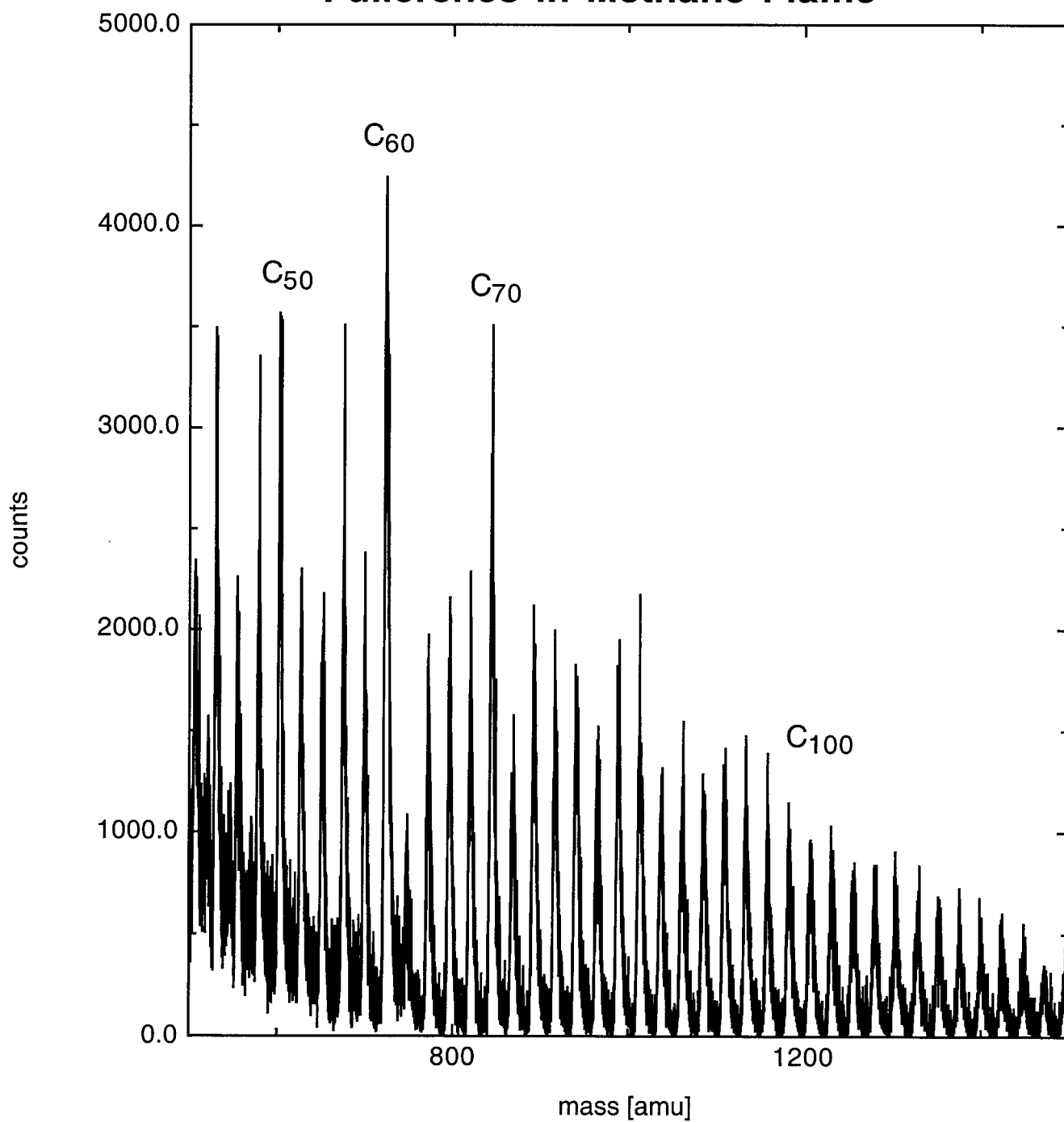


Fig. 6. Fullerenes extracted from a methane flame.

# Fullerenes and Soot Particles in Methane Flame

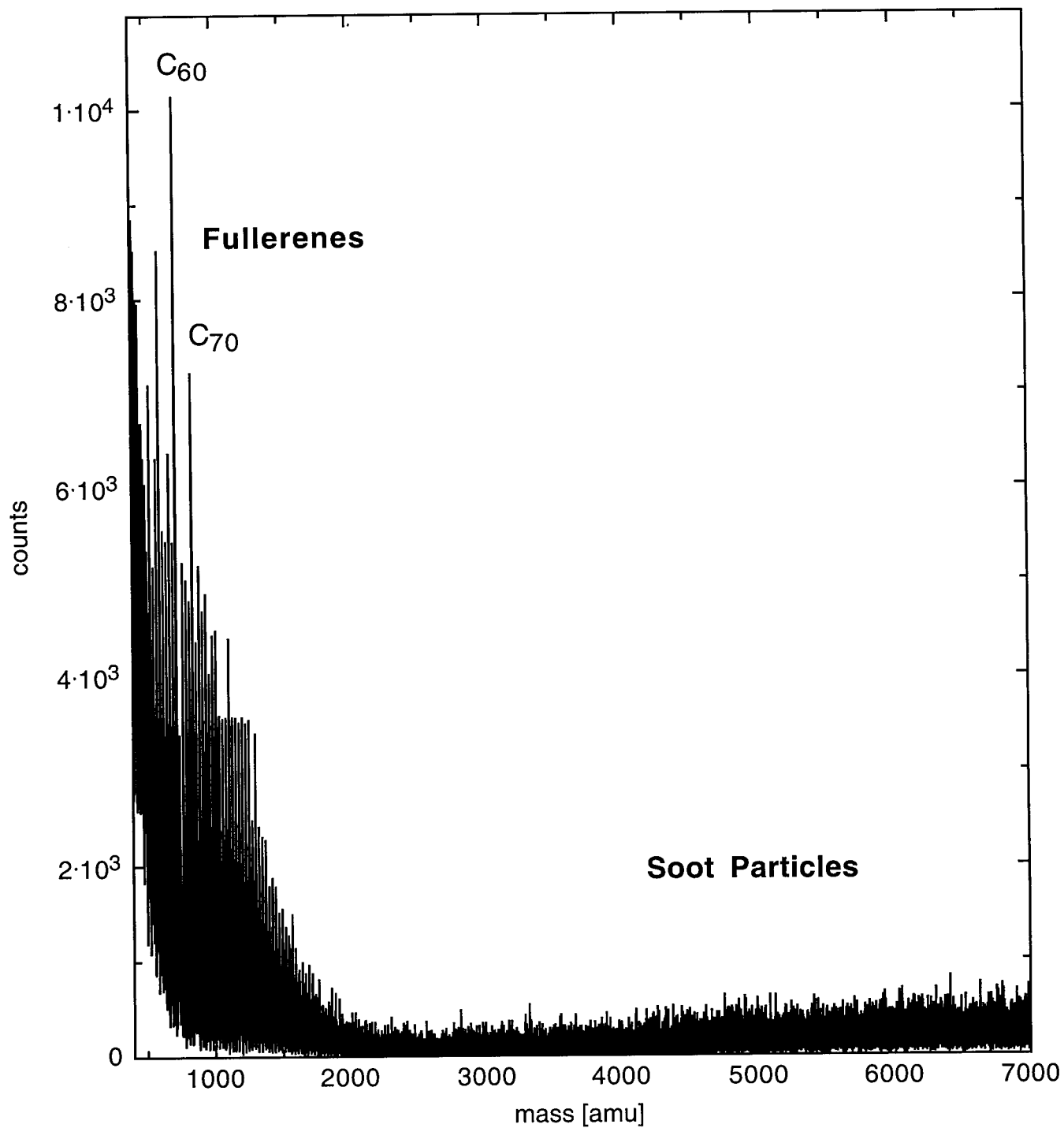


Fig. 7. Fullerenes and carbon soot particles extracted from a methane flame.

# Fullerenes and Soot Particles in Methane Flame

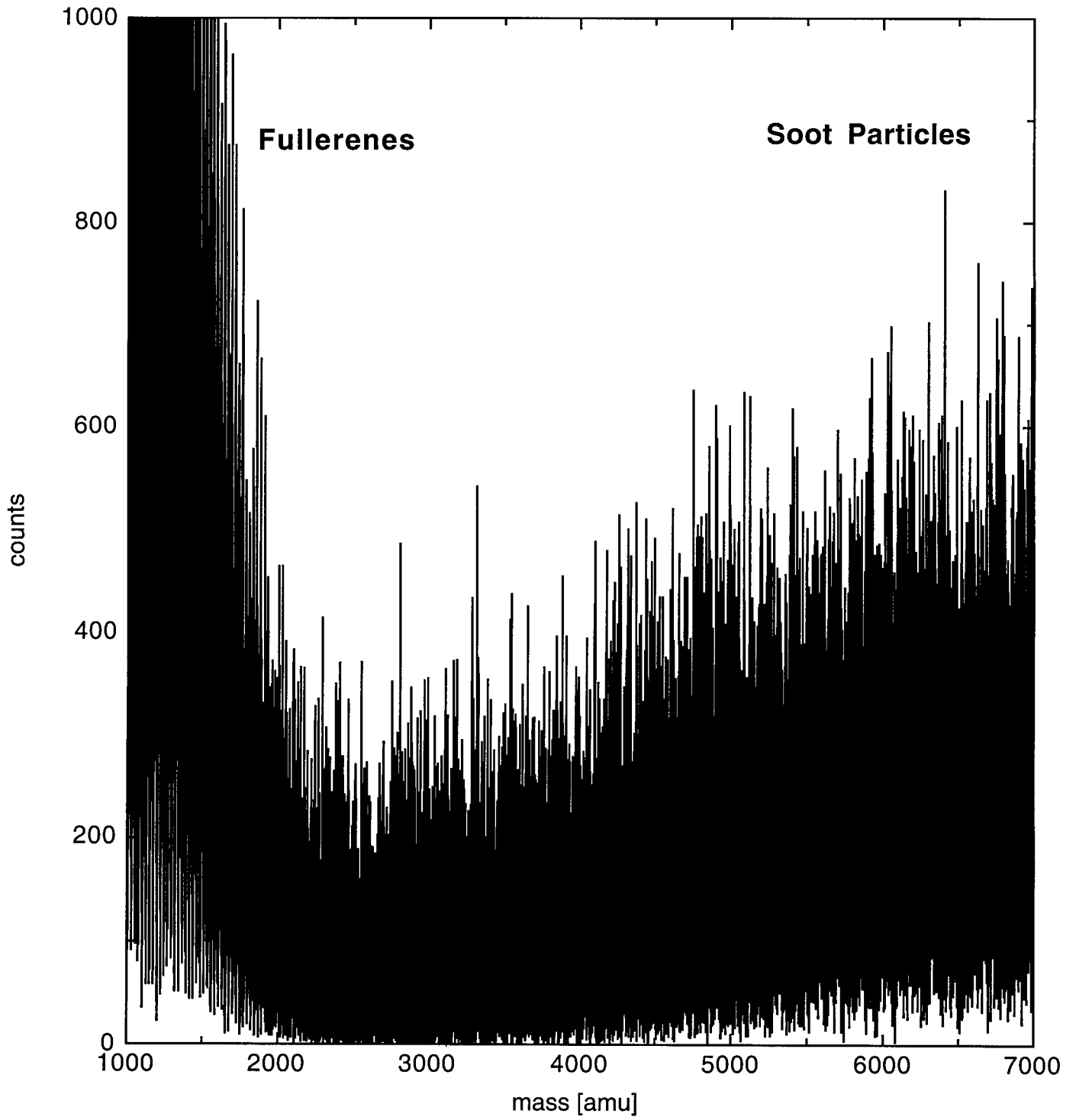


Fig. 8. Fullerenes and carbon soot particles; part of the mass spectrum from methane flame.