

Thermographic Analysis of Known Organic Substances

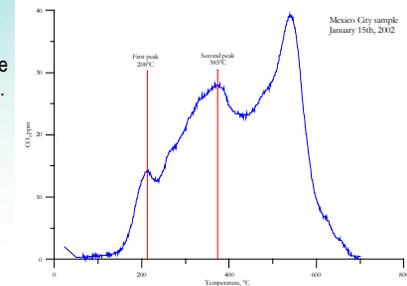
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1. Introduction

Evolved Gas Analysis, EGA, is a common procedure to estimate the amount of organic and elemental carbon content in urban aerosols. This technique relies on the oxidation process that occurs when a sample is heated in a furnace at controlled temperature and the emitted carbon is converted to carbon dioxide. Many thermograms have two main peaks that represent groups of organics. Temperature range 1 is between 200-300°C and is related to more volatile compounds with higher vapor pressures or lighter molecular weights. The second peak occurs in the temperature range between 300 and 400°C and is related to less volatile compounds. If the thermographic patterns can be linked to specific functional groups of organics, this will provide valuable information about the sources and evolution of ambient organic aerosols.

The results presented here are from a study to evaluate the thermographic patterns of some organic substances commonly found in urban emissions and to identify features in the thermograms that are related to the functional group of an organic compound.



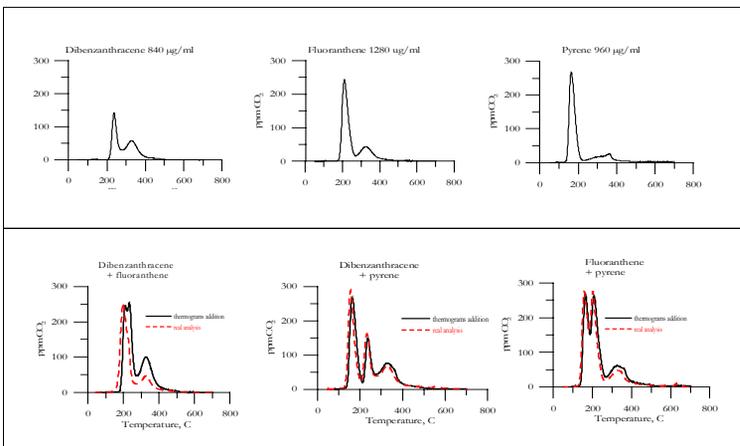
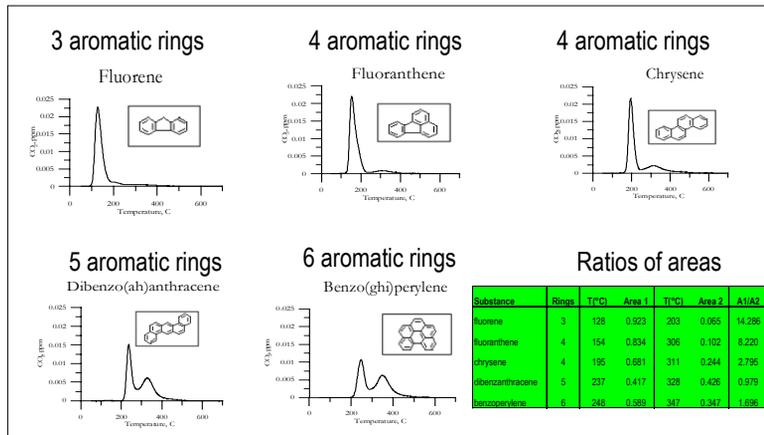
2. Shapes of thermograms based on the number of aromatic rings

2.1 Methodology

The organic samples were prepared in dichloromethane or toluene solutions. A total of 25 organic compounds and mixtures were analyzed. These substances were chosen and classified by functional groups like aliphatics, aromatic carboxylic acids and polycyclic aromatic hydrocarbons (with 3 to 6 rings in the internal structure). The thermograms are normalized by their total area in order to compare shapes, regardless of the absolute magnitude.

2.2 Results

The figures to the right show the thermograms, normalized by their area, of compounds with different aromatic rings. All these compounds, regardless of the number of rings, have their primary peaks in temperature range 1. The amount of carbon found in temperature range 2 increases with the number of rings in the organic molecule. The table summarizes the main characteristics of each thermogram.



3. Thermograms of Organic Mixtures

3.0 Motivation

Ambient samples are mixtures of a number of organic compounds. Hence, studies were done to evaluate if mixtures of pure compounds would behave in a predictable manner, i.e. if the thermographic patterns are additive or if combining functional groups changes the subsequent behavior during heating.

3.1 Methodology

The pure compounds were mixed, two at a time, and thermograms were generated. The shapes of these thermograms were compared to the shape obtained by numeric addition of the thermograms of the individual compounds.

3.2 Results

The figures at the left are examples of thermograms from mixtures of three substances, taken two at a time. The thermograms in the bottom row are combinations of the compounds shown in the top row. In red are the thermograms of the mixtures and in black are the summations of individual thermograms. The shapes are virtually identical, indicating that the EGA accurately represents mixtures as well as individual components.

4. Discussion

The thermograms show an evolving second peak as the number of aromatic rings increase in the molecule. This is seen as an increase in the area under the curves around this peak and is possibly linked to an internal degradation of the substance or secondary reactions among the molecules. An analysis of mixtures showed that combinations of compounds during the EGA did not behave differently than predictions based on arithmetic addition of the individual compounds. This implies that the shapes that are evaluated from ambient samples, if there is not any internal interactions, can be interpreted as coming from specific mixtures of different organic compounds and are not distorted by the heating process in the EGA.

5. Summary

EGA has the potential to derive more than just the bulk organic and elemental carbon concentrations of ambient aerosols. The patterns of the thermograms carry information about the types of organic groups, as has been demonstrated with organic compounds commonly found in the urban environment. A great deal more work is needed to relate thermographic patterns to the mixture of compounds that form the aerosol. These preliminary results suggest, however, that thermographic analysis should be further exploited to better understand the properties of aerosols.

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