

Characterization of the volatile fraction of laboratory-generated aerosol particles by Thermodenuder-Aerosol Mass Spectrometer coupling experiments

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Introduction

Volatility of aerosol particles is one important factor to determine their influences on global climate change and adverse impacts on human health. The most common device for volatility measurements is the thermodenuder (TD). So far, the instruments, which have been combined with a TD, are able to provide indirect information about the chemical composition of particles, but can not directly detect the changes in their chemical composition after being heated. In order to investigate aerosol particles with regard to their volatility and chemical content, a TD combined with an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Jayne et al., 2000 and DeCarlo et al., 2006) was used to measure the laboratory-generated aerosol particles in this study. The goals are to show if some molecules changed during the heating but do not completely evaporate and try to find the potential candidates for non-volatile material in aerosol particles observed in the field measurements (Wehner et al., 2005).

Experimental

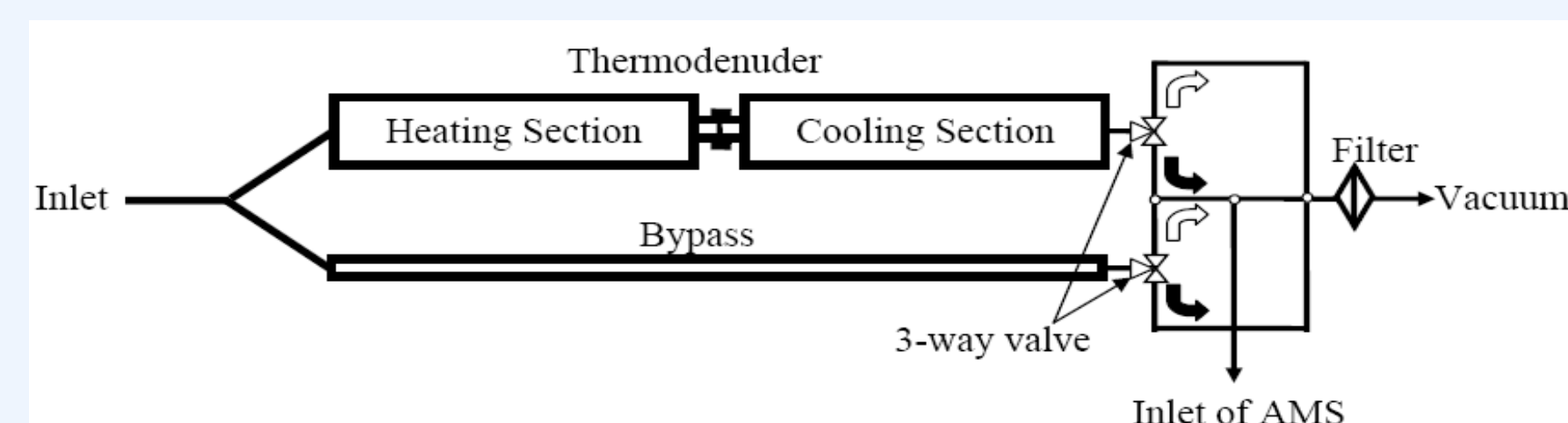


Figure 1: Schematic diagram of the setup for AMS coupled with TD

Figure 1 shows the schematic diagram of the setup for AMS combined with TD. The TD was operated at a flow rate of 0.6 l min⁻¹ and at temperatures up to 300°C. The residence time of particles in the heating section was approximately 9s.

By switching the two 3-way valves, the particles entering into the AMS can be either heated (with TD) or unheated (without TD). A detailed description of the TD is given in Wehner et al. (2002).

Ammonium sulfate particles were measured first and used to test the performance of the setup. In the next step, organic acids of atmospheric interests including humic, fulvic, succinic, methylsuccinic, fumaric, α-ketoglutaric, and glutaric acid particles were investigated.

Mass Fraction Remaining

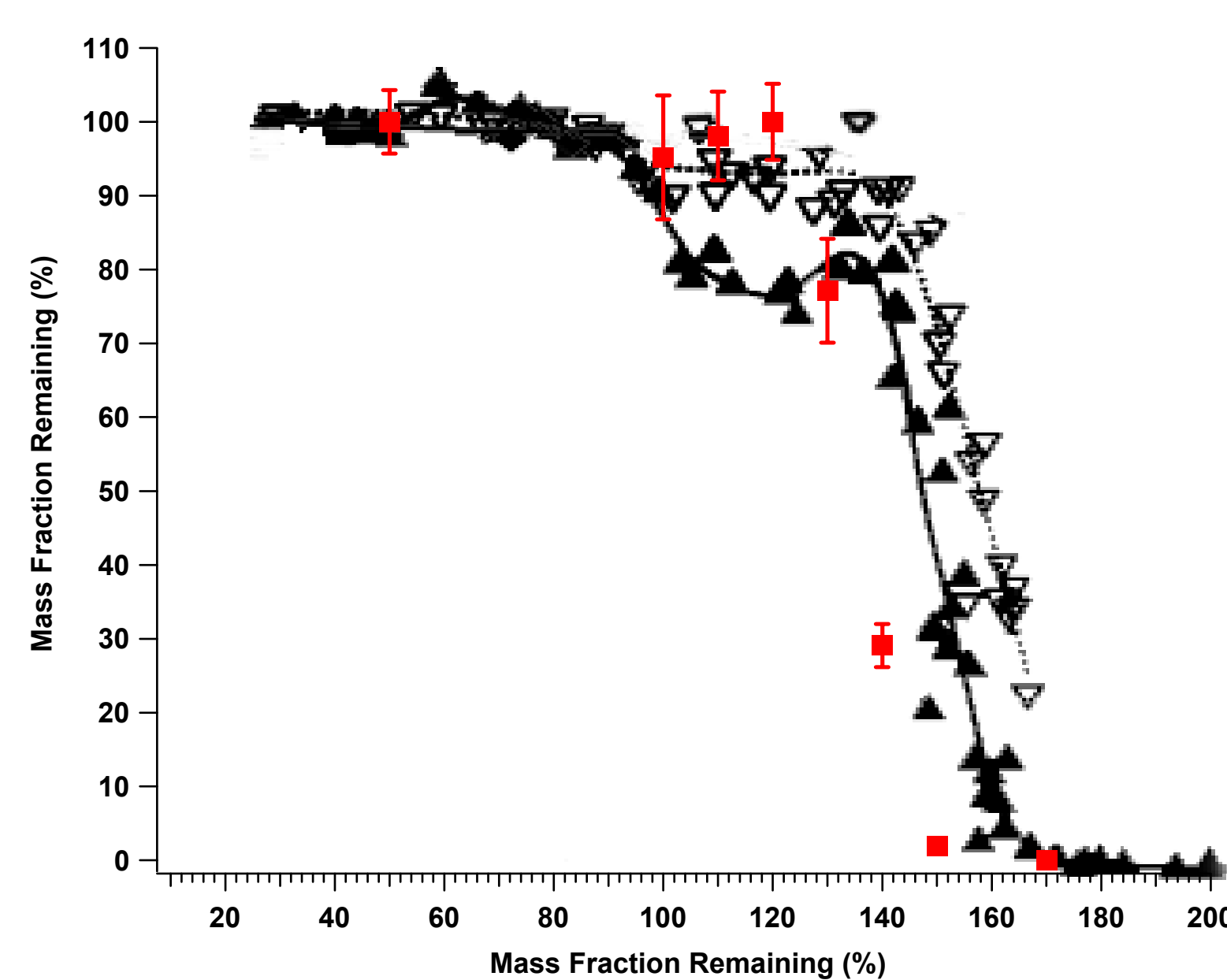


Figure 2: Mass fraction remaining of ammonium sulfate particle as a function of TD temperature (in black Huffman et al. 2008)

The remaining mass fraction (MFR), which is defined as the ratio of mass concentration at a given temperature to that at room temperature, is used to represent the volatilization of aerosol particles. Figure 2 shows the MFR of ammonium sulfate particles as a function of TD temperature. Above 120°C, the MFR decreases rapidly with increasing temperature and is nearly zero at 150°C. Recently a similar setup was used by Huffman et al. (2008), showing that the temperature, at which laboratory generated ammonium sulfate vanished (about 160°C) is slightly higher compared with this study.

Figure 3 shows the thermograms of humic acid, fulvic acid, and succinic acid particles. At 300°C, the MFR for humic, fulvic, and succinic acids are 58%, 47%, and 83% respectively. Other dicarboxylic acids including methylsuccinic acid, fumaric acid, α-ketoglutaric acid, and glutaric acid are more volatile than succinic acid and completely evaporate around 60°C.

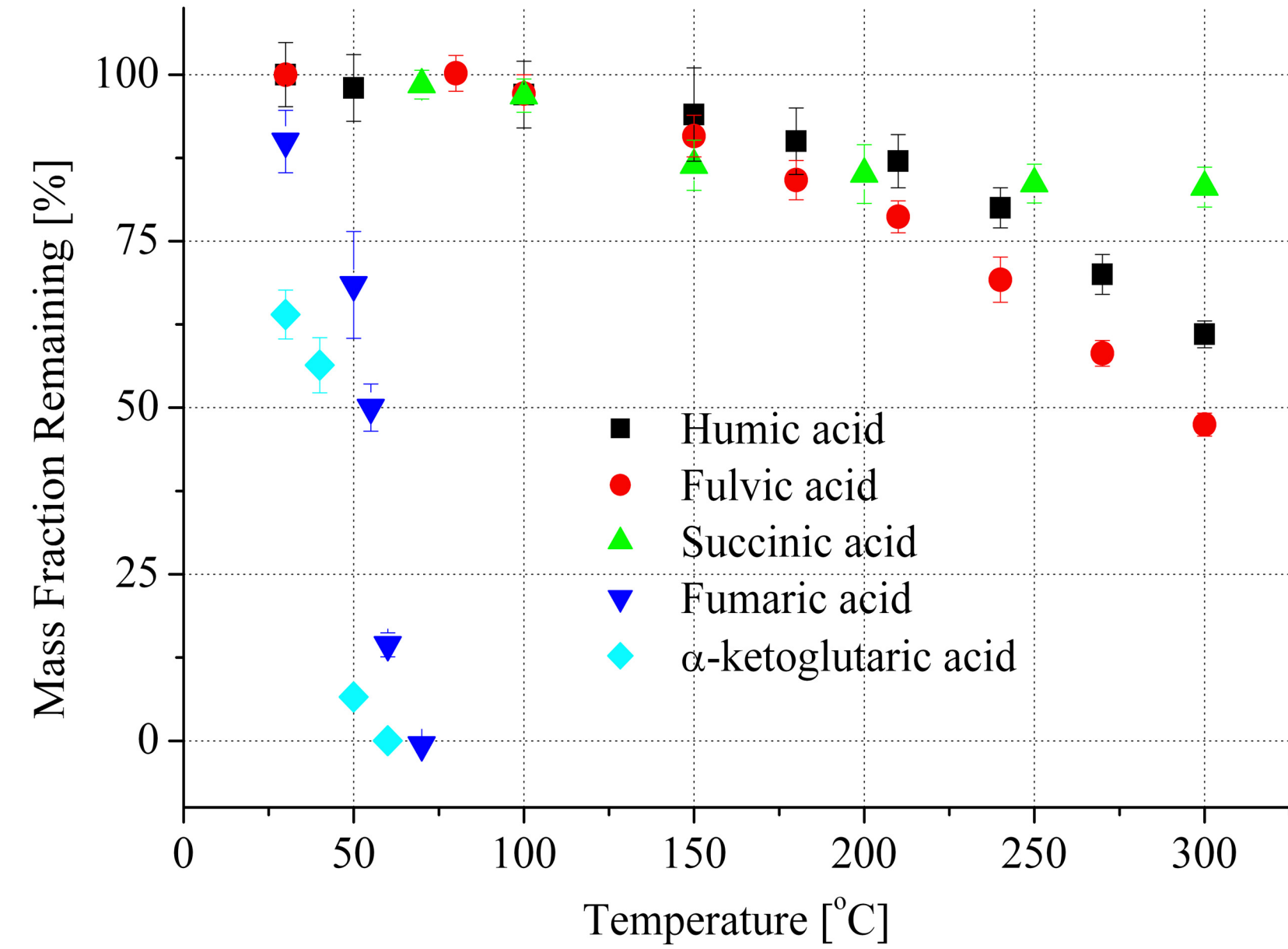


Figure 3: Mass fraction remaining of organic acids as a function of TD temperature.

Mass spectra analysis

Mass spectra of succinic, humic, and fulvic acids, which are normalized to the total organic signal derived from AMS at room temperature and 300°C, are shown in Figure 4. Mass spectra for succinic acid at room temperature are similar to that at 300°C. Significant differences in mass spectra of humic and fulvic acids at room temperature and 300°C are observed.

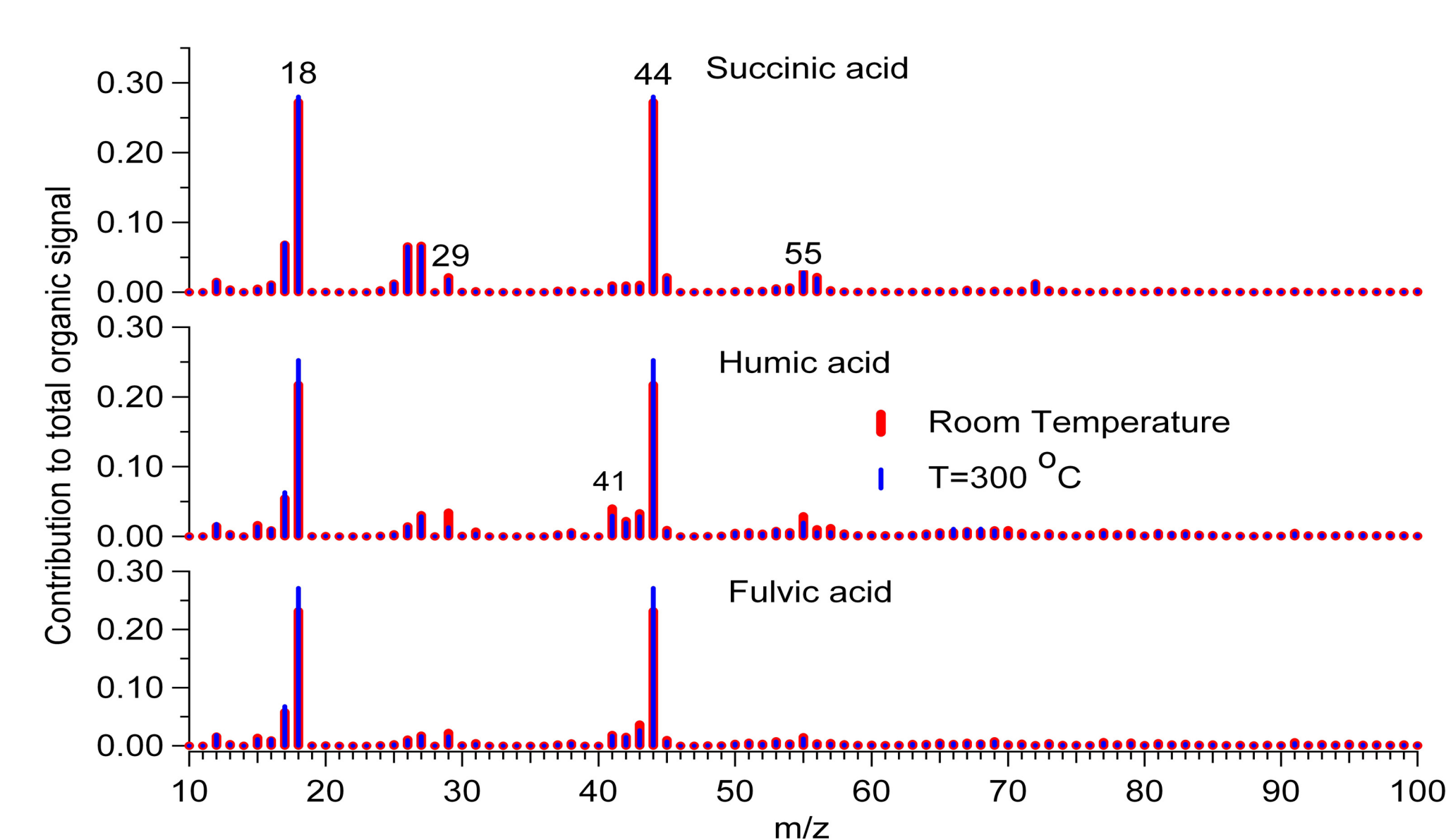


Figure 4: Mass spectrum of humic, fulvic, and succinic acids at room temperature and 300°C

Figure 5 shows contributions of the major mass fragments in mass spectra of humic and fulvic acids to the total organic signal as a function of temperature. These results indicate that changes which appear in the molecules of humic and fulvic acids are different after being heated to different temperatures.

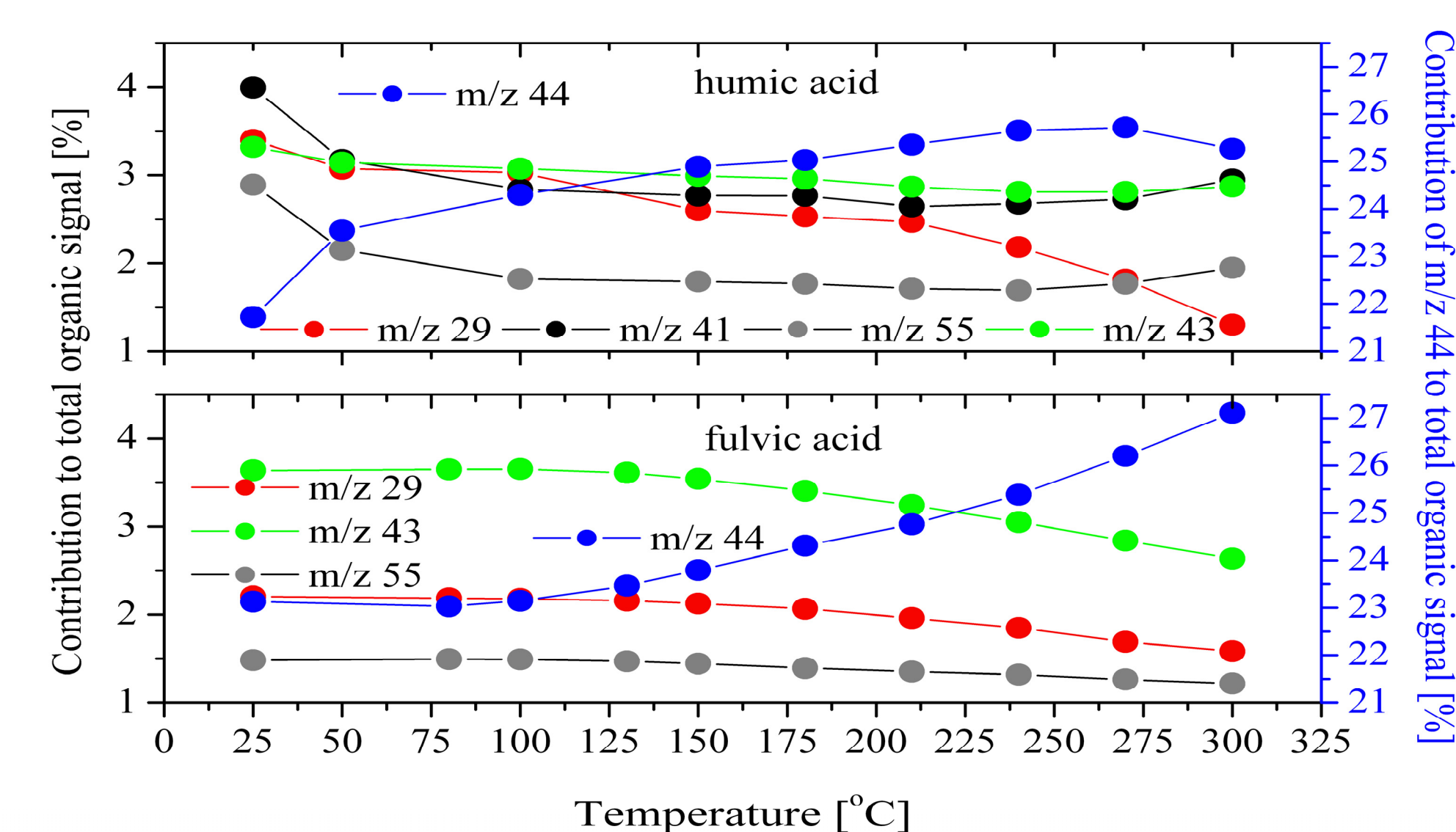


Figure 5: Contributions of the major mass fragments to total organic signal for humic and fulvic acids as a function of TD temperature

High resolution mass spectra

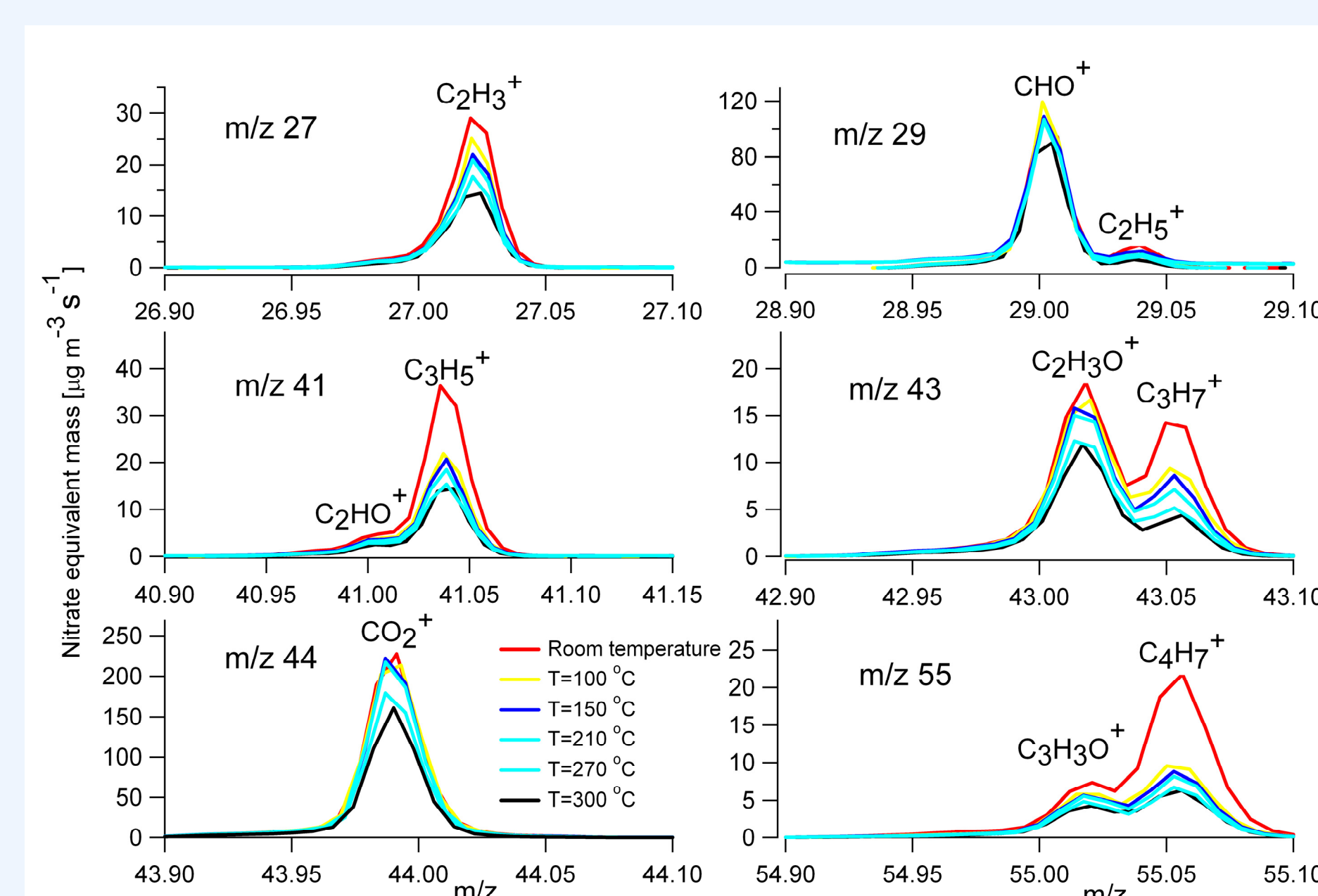


Figure 6: High resolution mass spectra at m/z 27, 29, 41, 43, 44, and 55 for humic acid

Figure 6 shows high resolution mass spectra of six major nominal masses of humic acid for different temperatures. The mass concentrations of the C₂H₃⁺, C₂H₅⁺, C₃H₅⁺, C₃H₇⁺, and C₄H₇⁺ fragments at room temperature are considerably lower than those at 100°C. The mass losses at 100°C are most likely due to the evaporation of small organic molecules and decomposition of aliphatic groups. The significant changes in mass concentrations of CO₂⁺ and CHO⁺ fragments were observed above 210°C, suggesting that the decarboxylation of humic acid occurred at higher temperature.

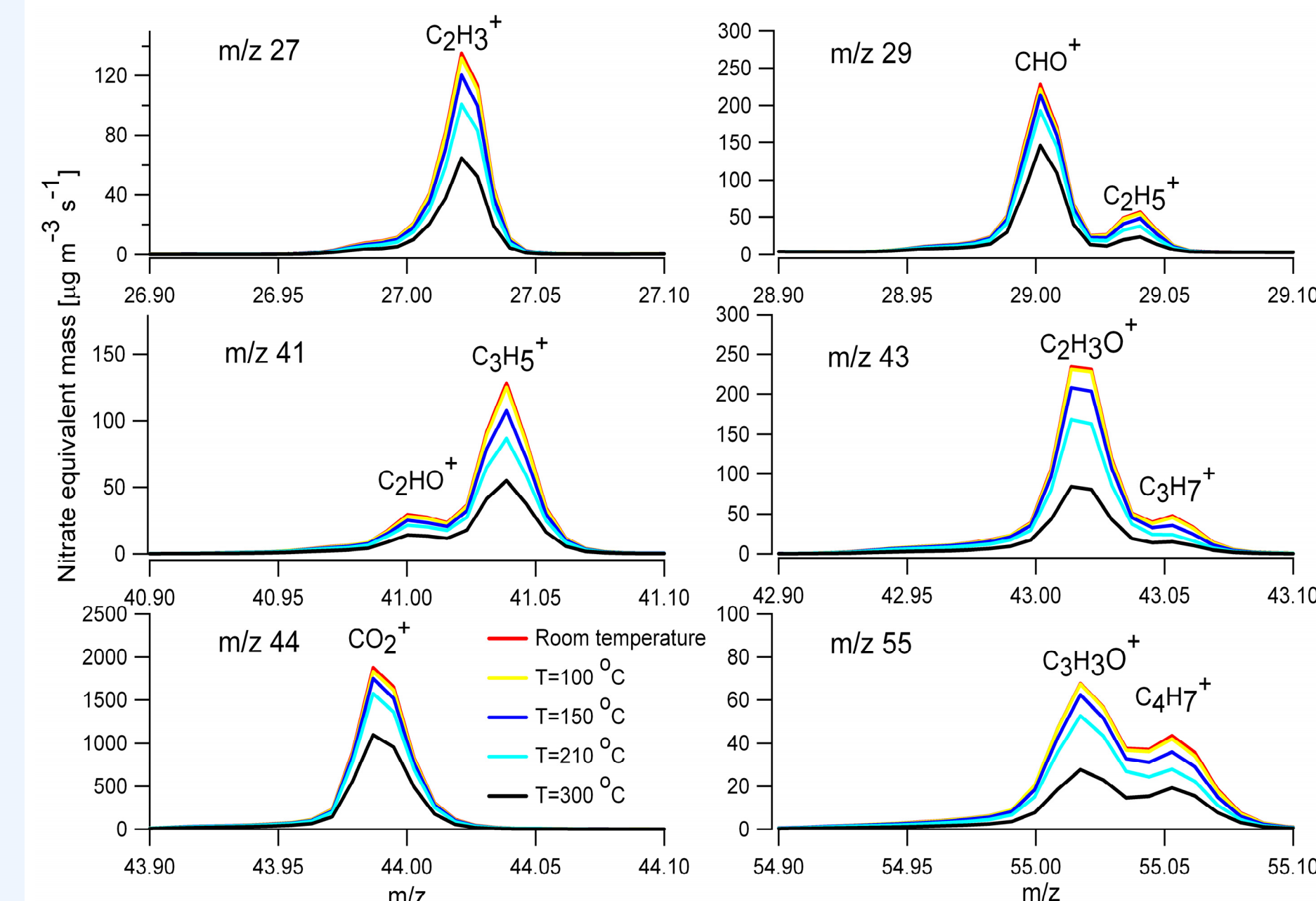


Figure 7: High resolution mass spectra at m/z 27, 29, 41, 43, 44, and 55 for fulvic acid

High resolution mass spectra of the six major nominal masses of fulvic acid at different temperatures are shown in Figure 7. The high resolution mass spectra at room temperature are similar to those at 100°C. A relatively rapid loss of all fragments was observed above 150°C. In contrast to humic acid, all major fragments of fulvic acid show more uniform reductions with increasing temperature, indicating that the structural changes in fulvic acid after being heated are more homogeneous in the 100-300°C temperature range.

Summary

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) combined with a thermodenuder (TD) was used to investigate the laboratory-generated aerosol particles with regard to their volatility and chemical information. Organic compounds have been measured including humic acid, fulvic acid, succinic acid, methylsuccinic acid, fumaric acid, α-ketoglutaric acid, and glutaric acid. Among them, humic, fulvic, succinic acids are non-volatile at 300°C. Those non-volatile organic acids may be relevant to the atmosphere. Comparisons of mass spectra at different temperatures showed that there are no changes in mass spectra of succinic acid after being heated. However, the significant differences in mass spectra of humic and fulvic acids are observed, indicating that their molecules changed during or after volatilization. The different mass spectra for humic and fulvic acids before and after TD also suggest that one should be careful in interpretation of volatility measurements because some molecule structures may change after being heated, especially for the non-volatile multifunctional compounds.

References

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