Investigation of Sulfur Allotropes with Thermal Analysis – Single Photon Ionization Mass Spectrometry

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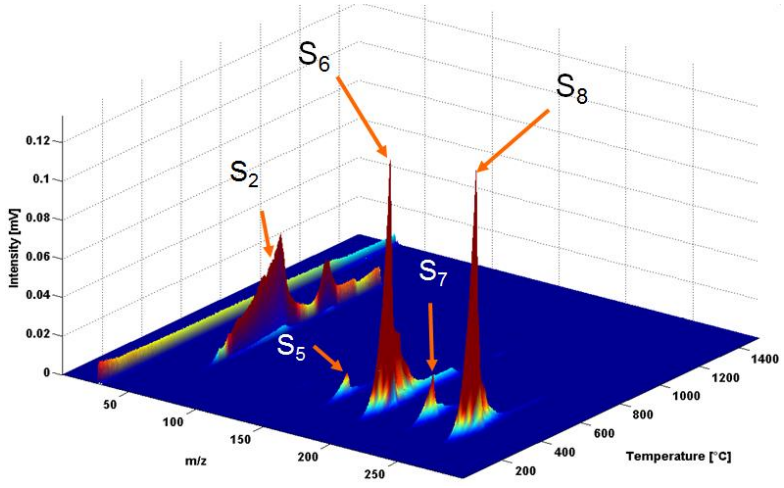
The connection of a simultaneous thermal analyzer (STA) and mass spectrometry (MS) is widely used for evolved gas analysis (EGA). The analyte transmission to the MS is strongly limited by the vapor pressure of the substances within the sample. One possibility to overcome this issue and enable the measurement of even low volatile compounds without any wall contact between the thermal balance and the ion source of the MS is a STA-MS with a skimmed interface. In this study, a modified Skimmer® system (Netzsch-Gerätebau GmbH, Selb) was applied to elucidate the composition of vapors of elements of the 15. and 16. periodic table group (phosphorus, arsenic, antimony, sulfur and selenium).

The original Skimmer® STA-MS system was modified by replacing the quadrupole mass analyzer with a single photon ionization time-of-flight mass spectrometer (SPI-TOFMS). The advantages of a fast modern time of flight mass analyzer are increased time resolution and sensitivity [1].
In most cases, electron ionization (EI) with standard kinetic electron energy of 70 eV is applied. Due to the high excess energy compared to the ionization energies of the analytes, fragment peaks are dominating EI mass spectra. The application of SPI allows soft ionization and fragmentation of the molecules is mostly avoided. The gathered molecule mass information makes mass spectra interpretation easier. Vacuum-ultraviolet (VUV) photons for SPI are generated by a commercial deuterium lamp (Heraeus Noblelight GmbH, Hanau).

Phosphorus, arsenic, antimony, sulfur and selenium exhibit a complex molecular composition of allotropes in the gas phase. In this study, the applicability of the system was tested especially on sulfur vapor. The vapor consists of all molecules with 2-8 sulfur atoms in temperature- and pressure-dependent equilibria (see figure below).
Another aspect of this study was the determination of the relative photoionization cross-sections of the allotrope modifications, which is crucial for their quantitation. For this purpose, a GC-EI/SPI-MS has been used. The same deuterium lamp as in the Skimmer® system was applied. The developed method allows quantitation of the different sulfur allotropes in the gas phase which is poorly investigated in the literature so far.



[1] Saraji-Bozorgzad et al. J Therm Anal Calorim (2011) 105:691-697 DOI 10.1007/s10973-011-1383-2