An Evolved Gas Analysis Method for the Characterization of Sulfur Vapor

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Abstract

In this study, thermal analysis coupled with soft ionization mass spectrometry was used for the speciation of sulfur vapor. Its investigation is still a challenge, since it exhibits a complex molecular composition. A thermal analysis – mass spectrometry system was equipped with a single photon ionization time-of-flight mass spectrometer (SPI-TOFMS). Single photon ionization is a soft ionization method which produces less or no fragments. Ionization is performed with vacuum ultraviolet (VUV) photons generated by an electron beam pumped excimer lamp (EBEL) and a deuterium lamp. The applicability of the developed system was demonstrated for the determination of sulfur vapor composition. Several allotropic modifications were detected in the gas phase depending on temperature. Since the ionization energies of the species are between 8.6 and 9.7 eV, soft ionization is crucial for this reason. Thermogravimetric and DSC data deliver additional information to the mass spectrometric data and enable the detection of allotropic transitions in solid and liquid phase.

Introduction

The vapors of the group 16 elements (sulfur, selenium, and tellurium) exhibit a complex molecular composition. The characterization of these vapors is still challenging. The vapor phase above a sulfur

melt sample contains different ratios of allotropic modifications in temperature and pressure dependent equilibria. Due to the lack of data gained with modern analytical techniques, "it is obvious that more work and new approaches" are necessary [1]. The computational evaluation of these vapors also triggers the need for new data on the vapor compositions.

There are some publications available on the speciation of vapor generated by heating elemental sulfur. The used analytical techniques are pressure and density measurements, different spectroscopic methods such as vibrational (Raman), UV-Vis spectroscopy or recently near edge structure (XANES) spectroscopy [2][3][4] and mass spectrometric methods. In the following, we detail the results on sulfur vapor achieved with mass spectrometric methods.

Sulfur vapor contains measurable quantities of several molecular cluster species of the formula S_n (n=1-10) [5], although the mass spectrometric evidence for S_9 and S_{10} in the equilibrium sulfur vapor is weak. The standard method for the mass spectrometric investigation of vapors is based on a Knudsen cell source whose effusing gases are ionized in the ion source of the mass spectrometer (Knudsen effusion mass spectrometry, KEMS). Berkowitz et al. [6] studied with KEMS elemental sulfur and sulfides (HgS, CdS, ZnS, FeS, SrS, CaS), since those decomposition upon heating produces sulfur vapor. Evolving species from the Knudsen cell were ionized by electron ionization (EI), the appearance potential of the evolving species was also established by reducing the ionization energy. They found that saturated vapor contains the molecules of S_2-S_8 and also detectable but insignificant amounts of S_9 and S_{10}. Mass spectrometers coupled with Knudsen cells use usually electron ionization, which makes it impossible to distinguish between parent ions and fragment ions of the different sulfur species. To overcome this issue, mass spectrometers with photoionization can be used. Berkowitz et al. described a 60°-sector mass spectrometer with light source and a 1 m vacuum-ultraviolet monochromator coupled with Knudsen cell [7]. They found that the ionization potentials of S_2-S_8 are in the range of 8.6 and 9.7 eV. The experimental apparatus was rather complicated and unique; no publications are available with a modern benchtop mass spectrometer.

Photoionization has its roots in the 1970´s and represents a fast developing area of mass spectrometry mirrored by a growing number of publications [8]. Photoionization belongs to the so called soft ionization methods: molecular radical cations (M+·) or -occasionally-characteristic high-mass fragments are obtained in the primary "physical" photo ionization process in contrast to hard ionization techniques where low-mass fragments dominate the mass spectra. This is mainly owed to the fact that the photon energies used for ionization are in the range of 7-12 eV which correspond to the typical ionization energies of organic molecules and also some inorganic compounds. Electron ionization with electrons of a kinetic energy of 70 eV causes a broader energy distribution in the formed molecular ions, resulting in a typically strong fragmentation (hard ionization). There are different types of photoionization depending on the photon source. The here used single photon ionization (SPI) is a rather universal ionization technique, which is based on a one-photon absorption/ionization process and performed with different kind of lamps (e.g. discharge lamps, electron beam pumped excimer light sources (EBEL)) or lasers [9], emitting in vacuum ultraviolet wavelength region.

There are two main options to couple mass spectrometry with thermal analysis devices. In most cases, transfer of the evolving gases from the thermal process is performed via a heated capillary. This method is usually performed with a deactivated fused silica capillary, where transfer times can lead to a delay in the detection of the evolving gases. The usual transfer line temperature is below 300 °C which does not allow the transfer of low volatile compounds. The TA-capillary-MS coupling is generally applied for the investigation of organic compounds, often applying SPI to gain fingerprint mass spectra [10][11] or with an additional GC step (TA-GC-MS) [12][13] for the better separation of highly complex matrices. A further disadvantage of the capillary coupling is that the evolving molecules often undergo decomposition or interactions take place in the capillary. Thus, it is obvious that another approach is necessary for the characterization of vapors of group 16. A real-time and wall-contact free sampling is possible by the skimmer inlet technology, which contains a second pressure reduction step [14] [15]. Transfer times are much shorter than with capillary coupling and

3

condensation is prevented. The skimmer coupling is usually achieved through a divergent nozzle and a conically distended aperture (skimmer) with an orifice positioned into the central part of the expanding gases. Nozzle and skimmer are either made of heat resistant metals for application temperatures up to 800 °C or alumina up to 1450 °C or glass carbon up to 2000 °C.

We tested the applicability of thermal analysis directly coupled with single photon ionization mass spectrometry (TA-Skimmer-SPI-TOFMS) for the characterization of sulfur vapor to overcome the usage of rarely available KEMS techniques. Another drawback of KEMS is that these devices are usually not available with soft ionization which is inevitable for the speciation of the sulfur modifications in the gas phase. In addition, we evaluated how far the developed method is suitable to determine the equilibrium composition of sulfur vapor.

Experimental

Instrumental setup

A commercially available thermal analysis – mass spectrometer system (STA 409 CD with QMS 403/5 Skimmer®-Coupling, Netzsch-Geraetebau GmbH, Selb, Germany) was modified. The quadrupole analyzer was replaced by an orthogonal acceleration time-of-flight mass spectrometer (CTOF, Tofwerk, Thun, Switzerland). The scheme of the system is depicted in **Fig. 1**. The instrumental setup was described in detail previously [16]. The Skimmer® coupling enables the on-line wall-contact free analysis of the evolving gases, which will be transferred via an interstage vacuum chamber (40 mbar) from atmospheric pressure of the thermobalance into the high vacuum of the mass spectrometer. Time-of-flight mass spectrometers are able to measure the whole mass range to achieve fingerprint-like-mass-spectra, which is not possible with quadrupole mass analyzers. It is especially useful for the investigation of complex gas mixtures.
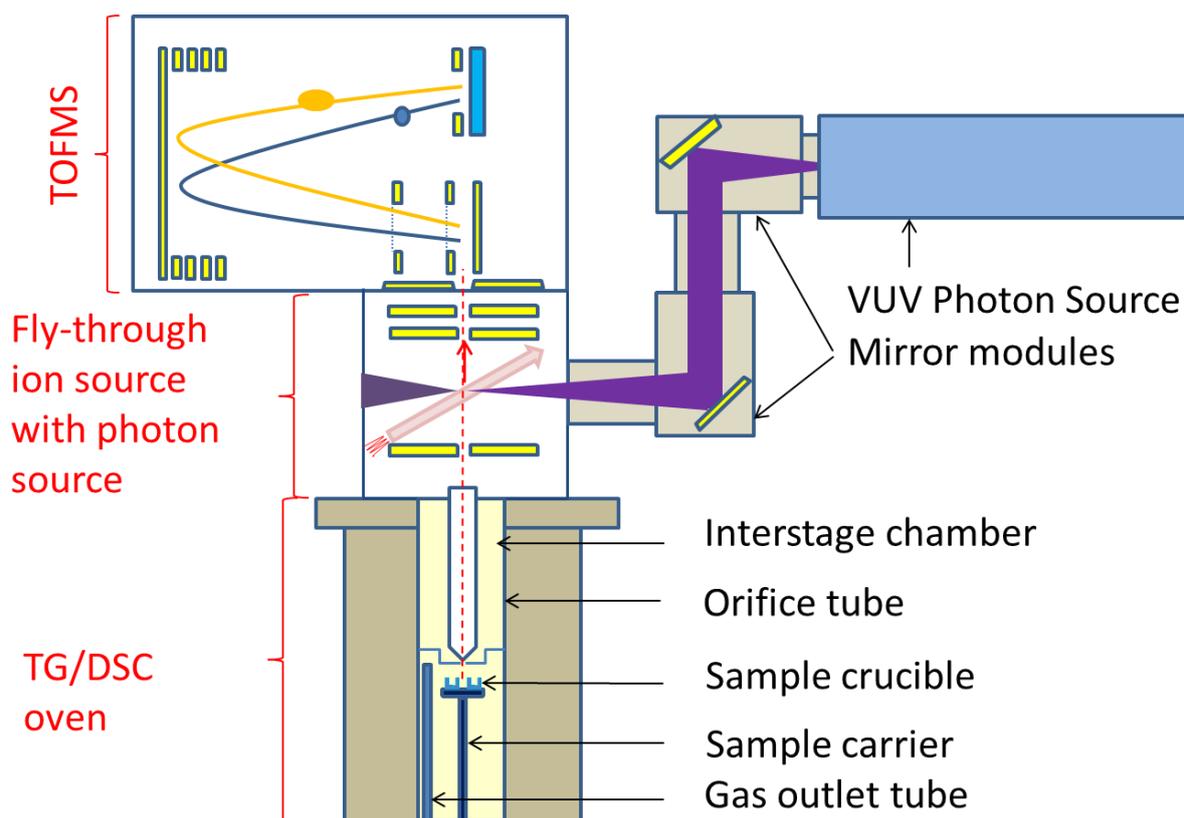
Fig. 1 Scheme of the modified QMS 403/5 Skimmer® device hyphenated with an orthogonal acceleration time-of-flight mass spectrometer and VUV photon source for the soft ionization of evolved gases

The instrument described by Saraji-Bozorgzad et al. [16] was further developed. VUV light was focused with a mirror module containing two parabolic MgF_2 coated mirrors to enhance the performance of photo ionization. Furthermore, we tested different lamps. In the homebuilt electron beam pumped excimer light source (EBEL) [17], the excimer process generating VUV photons and the energetic electrons are separated with a silicon nitride foil in space. Depending on the rare gas or gas mixtures, different photon energies can be achieved for the ionization. In this study, argon was used, whose center wavelength is at 126 nm, corresponding to 9.8 eV (**Fig. 2a**). Another applied lamp was an easy to handle, air-cooled deuterium lamp (Hamamatsu Photonics K. K., Hamamatsu City, Japan). In discharge lamps, in contrast to the EBEL, energetic electrons are generated in the gas cell. Local maximum of the wavelength–irradiance function is at 122 nm which corresponds to 10.16 eV photon energy (**Fig. 2b**). The photon density emitted by the deuterium lamp is higher than by the EBEL light

source. Enhanced photon densities led to increased signal intensities. However, the emission spectrum of the EBEL exhibits a Gaussian distribution and intensity. The emission spectrum is more stable in time as well. Note that the mass spectrometer can be operated also with standard electron ionization, where the applied ionization energy is usually 70 eV.
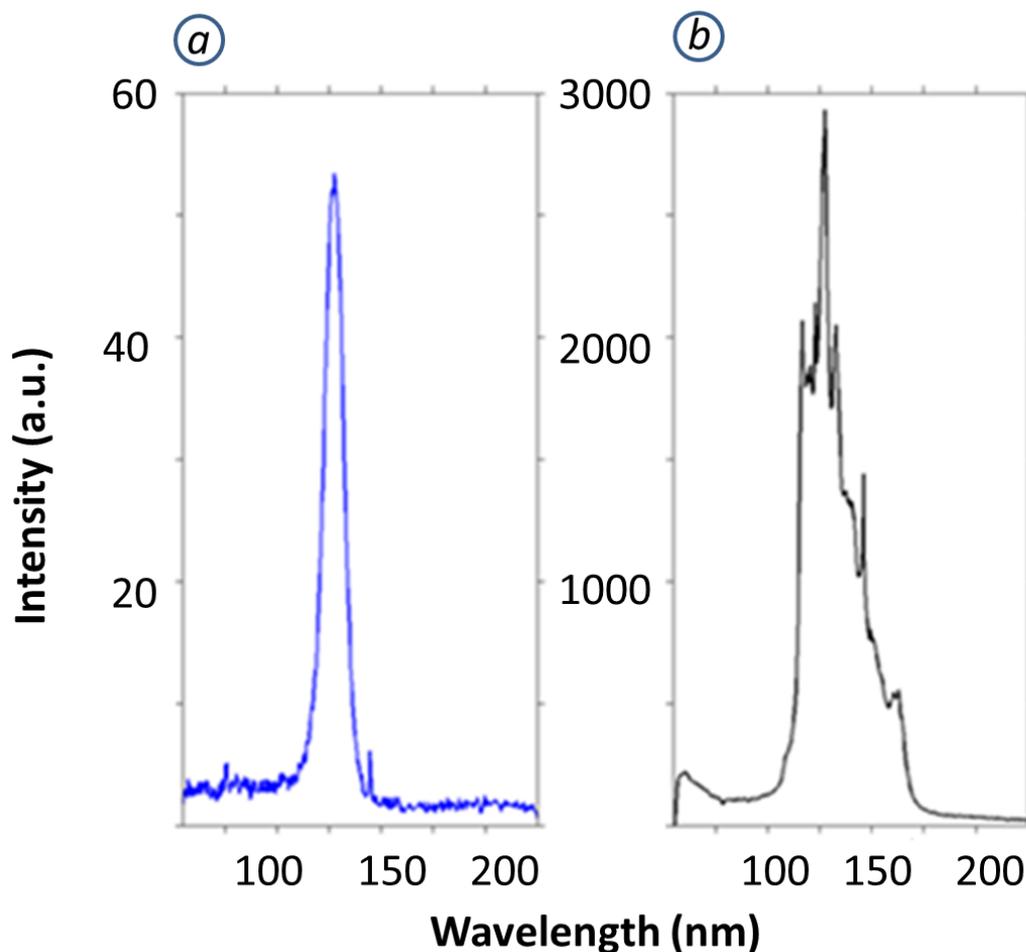
Fig. 2 VUV-emission spectrum of EBEL light source (a) and deuterium discharge lamp (b)

Measurement conditions

Measurement conditions for the sulfur samples were: heating rate: 10 °C/min 25-600 °C, purge gas: 30 mL/min N_2, protective gas: 30 mL/min N_2, weighing: 8-23 mg. Samples were placed in aluminum oxide crucibles, with a lid and a small pinhole in the lid. Furthermore, the suitability of the instrumental setup for the investigation of the equilibrium composition of vapors was tested. For this

reason, measurements with an isothermal temperature program were performed. Measurement conditions were: heating rate: 10 °C/min until 300 °C, followed by a 30 min isothermal segment, purge gas: 30 mL/min N_2, protective gas: 30 mL/min N_2. Sulfur was purchased from Sigma-Aldrich (99.5 %, Steinheim, Germany).

Results and discussion

In the following, TG/DSC-Skimmer-SPI-TOFMS results are presented in order to demonstrate the applicability of the developed system for the comprehensive investigation of sulfur, especially for the molecular composition of the vapor phase. Following data were obtained with the aforementioned deuterium lamp. First, we evaluated the necessity for the usage of soft ionization by comparing mass spectra gained during the TG/DSC measurements with different ionization energies. Soft ionization plays a crucial role in the characterization of sulfur vapor. **Fig. 3** depicts the combined mass spectra of elemental sulfur gained during a TA run and thereby demonstrates the differences between EI and SPI techniques. The SPI mass spectrum is depicted in **Fig. 3a**. The most intense peaks are S_6 and S_8, followed by S_7, S_5, S_2 even S_4 and S_3 can be detected in trace levels (not visible in the spectrum). In **Fig. 3b**, the EI mass spectrum shows the increased fragmentation due to the higher ionization energy. The main fragment in this case is S_2, the other molecules S_3-S_8 can be hardly seen in the mass spectra. This comparison between the ionization techniques shows that conventional EI is not suitable for the characterization of sulfur vapor, since the assignment of the EI fragments to the respective species is not possible.
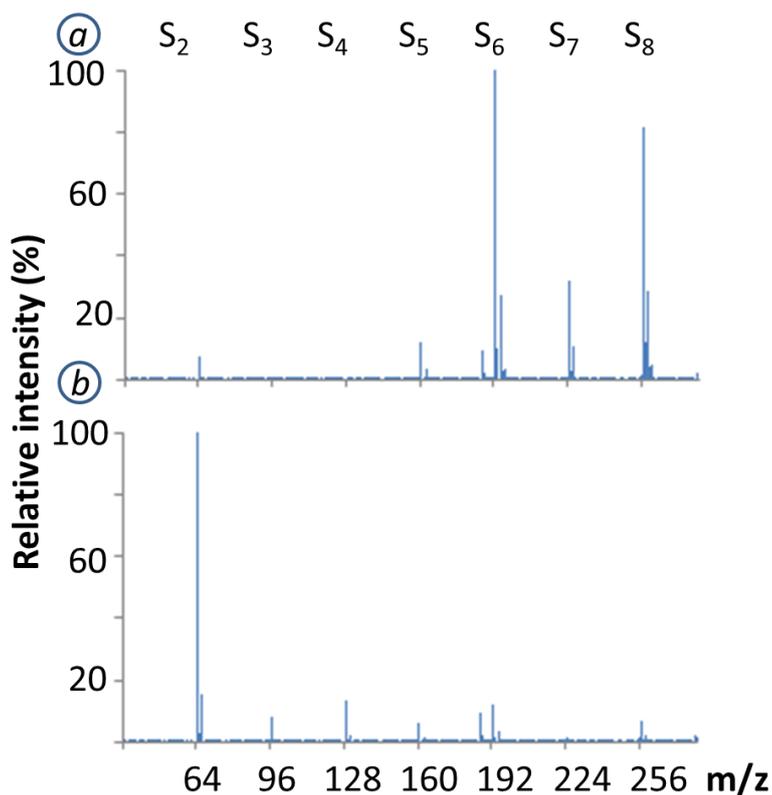
Fig. 3: Mass spectra of sulfur vapor with different ionization techniques: soft ionization performed by deuterium light source (a) 70 eV standard electron ionization (b)

Fig. 4 shows the mass traces with the corresponding TG/DSC curves. The TG curve shows a typical evaporating behavior, on the DSC curve, besides melting and evaporation, allotropic transitions can be followed as well. The first two partly resolved endothermic peaks (onsets 103.5 °C, 119.4 °C) belong to the reversible transition into ß-sulfur and the melting, the third peak is the endothermic polymerization peak, belonging to the so called λ-transition, (onset 167.3 °C) where viscosity is dramatically increasing due to the formation of polymers, the fourth peak beginning at about 300 °C belongs to the evaporation of the sample [18]. In the 3D plot, on the axes, the m/z value, temperature and signal intensity can be seen. The most intense species are S_6 and S_8, followed by S_7, S_5, S_2, and S_4, S_3 can be detected in trace levels.
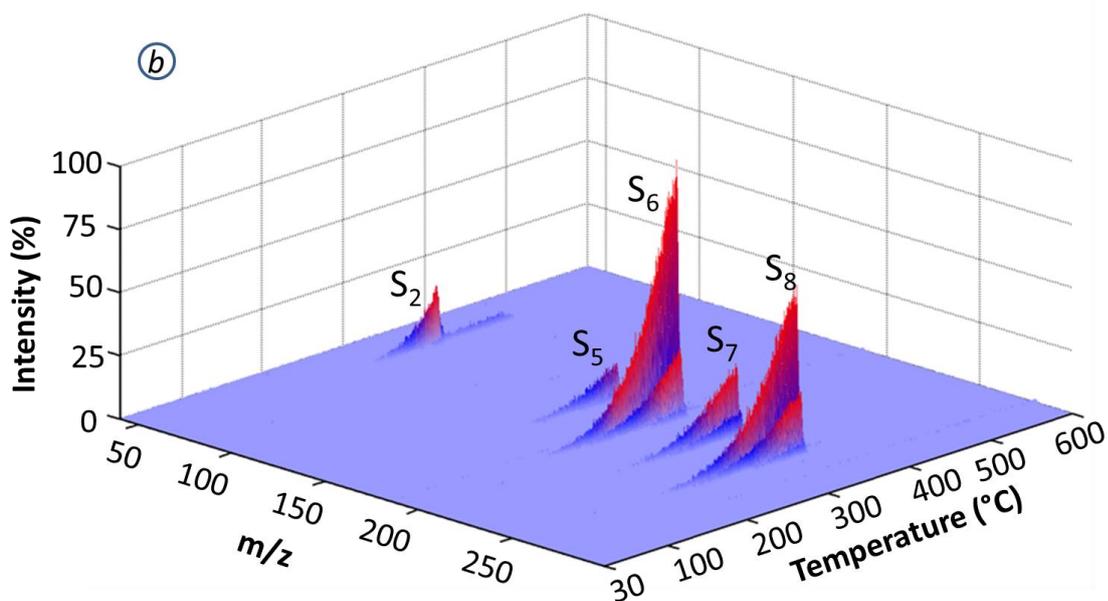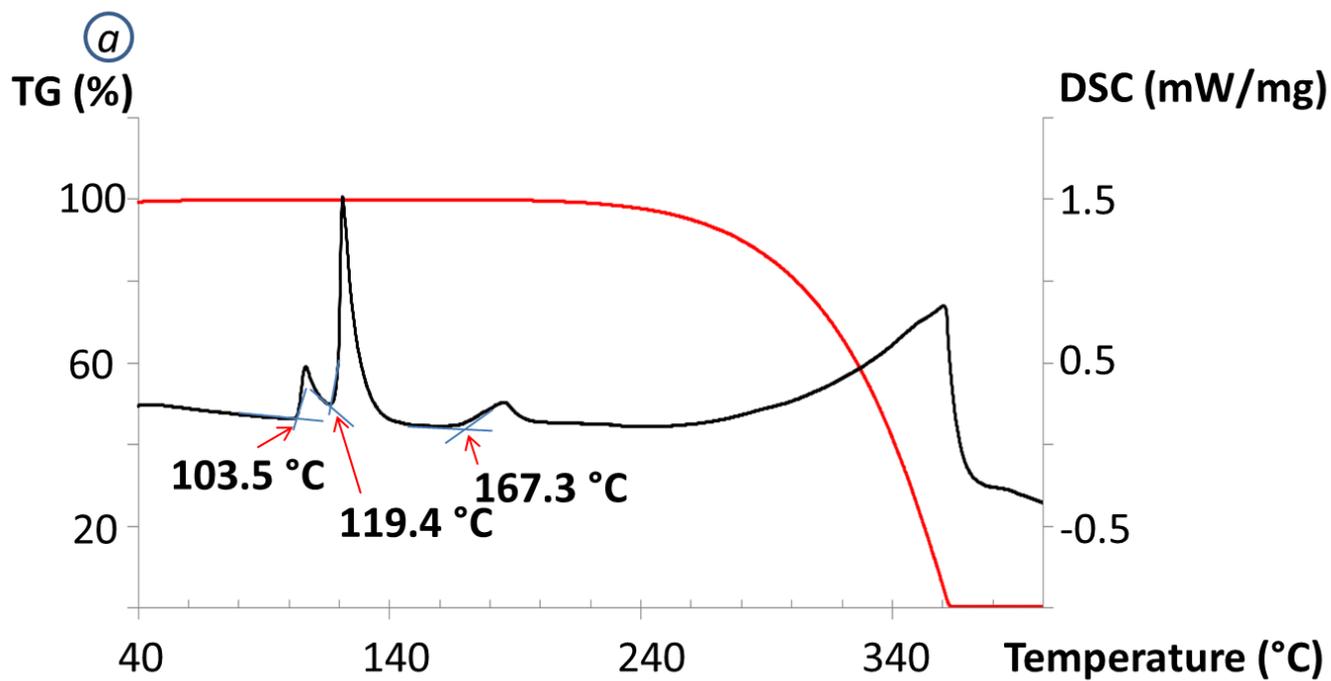
Fig. 4 TA-Skimmer-EI/SPI-TOFMS results for elemental sulfur: TG/DSC curves (a) m/z – temperature – intensity plot (b)

The composition of the vapor phase above the sulfur melt can be calculated from the mass spectrometric traces. During the calculation, also isotopes have to be considered. **Fig. 5** shows the

molar percentages of the different allotropic modifications of sulfur vapor between 200 °C and 350 °C. The main species are $S_8 > S_6$, however there is an increasing ratio of S_6 at higher temperatures. The amount of S_2 starts to increase fast at ~280 °C and reaches ~1 mol% until 350 °C.
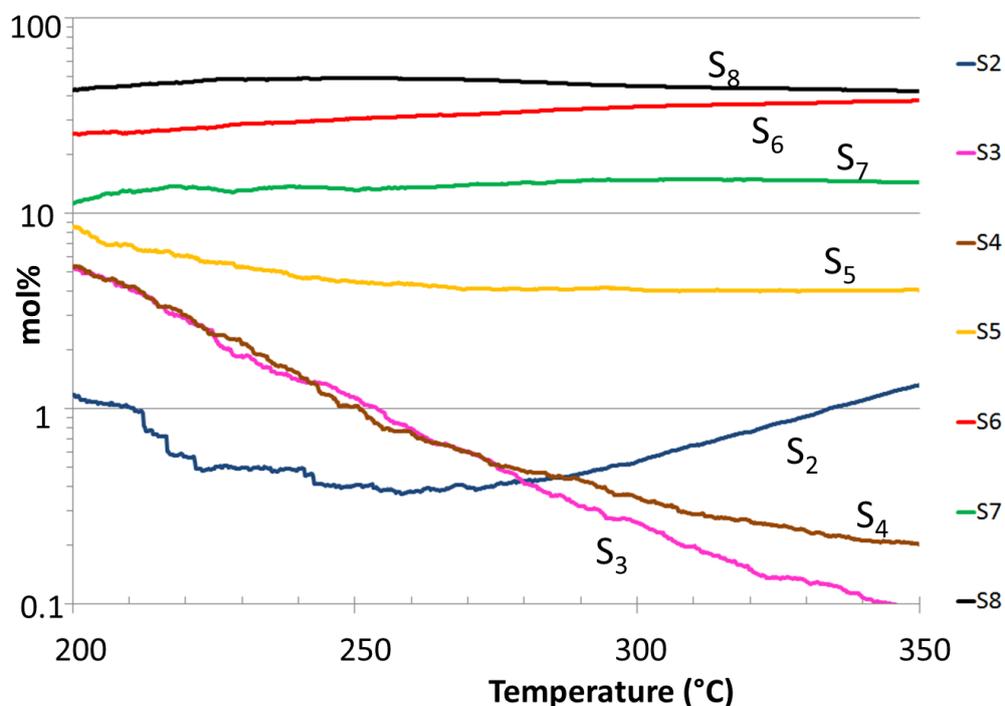
Fig. 5 Composition of vapor above a heated sulfur sample

Measurements with an isothermal segment were done to inspect the applicability of the system for equilibrium sulfur vapor. The mol%-temperature diagram and the total ion count (TIC) are depicted in **Fig. 6a**; **Fig. 6b** shows the TG/DSC curves of the investigated sulfur sample. Mass spectrometric data show that the sulfur species S_2-S_8 are detectable effusing through the pinhole from the sample crucible and the equilibrium composition occurs fast after reaching 300 °C and this state is stable during the isothermal segment of the measurement. Comparing the calculated mol% values with literature data (**Table 1**), they are in good agreement for all species. We observed the biggest difference for S_2, but literature [6,19] is also inconsistent for this molecule. Photoelectrons can also cause this discrepancy. The equilibrium state is also proven on the corresponding TG and DSC curves, according to **Fig. 6b**, mass loss and enthalpy is constant during the 300 °C segment.
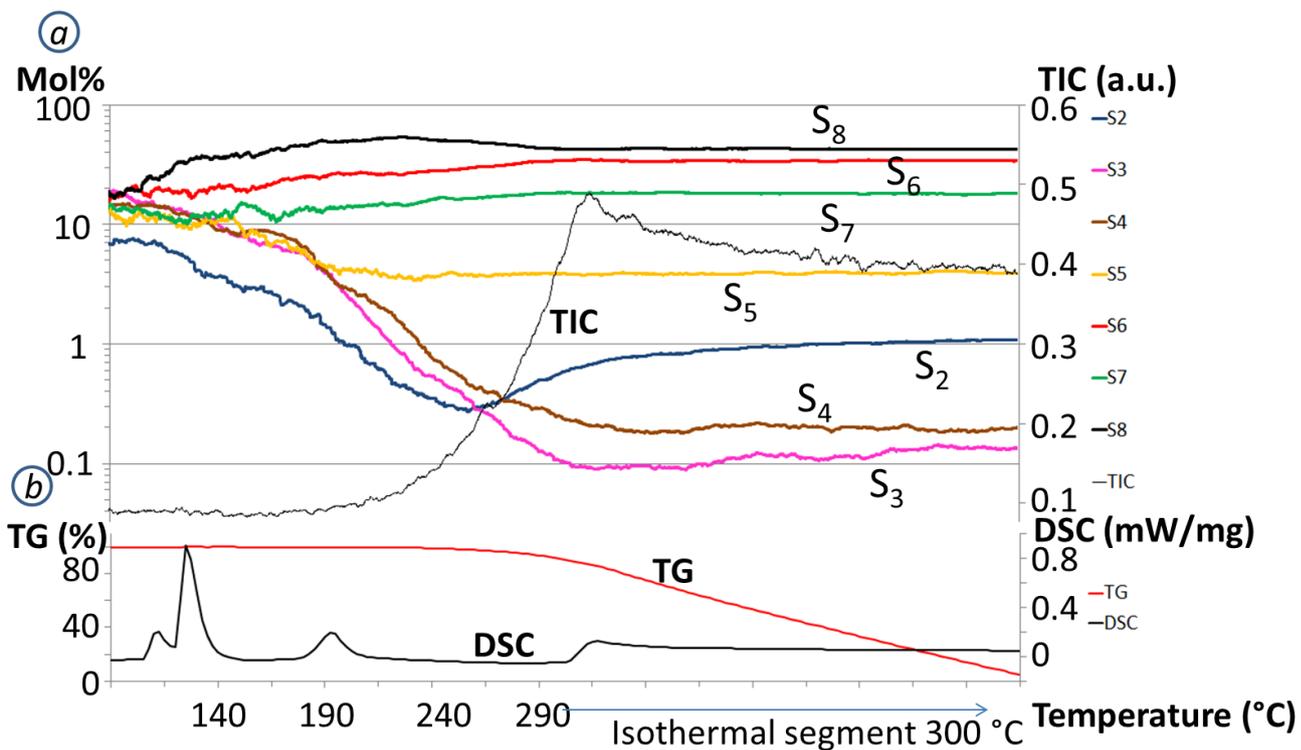
Fig. 6 Equilibrium sulfur measurement: mol% and total ion current (TIC) (a) TG and DSC curves (b)

Species	mol% at 300 °C	Literature 1 [6]	Literature 2 [19]
S_8	45.5±4.1	45	45
S_7	18.5±1.7	20	30
S_6	30.8±3.9	30	20
S_5	4.0±0.7	3	2
S_4	0.2±0.1	0.4	0
S_3	0.1±0.1	0	0
S_2	1.0±0.1	0.4	0.2

Table 1 Molar percentages of sulfur species determined during the isothermal segment calculated by 4 independent measurements

The probability of photoionization is related to the photoionization cross sections, which has to be considered for the more exact relative quantification of the sulfur species. No experimental data are available in the literature for the cross sections of S_2-S_8, Guthrie et al. [20] assumed that the effective ratio of the ionization cross sections is about $\sigma(S8)/\sigma(S2)=2$ and the intermediate species can be interpolated. The only way to estimate the relative cross sections are quantum chemical calculations, which will be done in the near future. During the calculations, the lamp spectra have to be

considered as well, since the different wavelengths of the ionizing photons lead to different cross section of the same molecule with different lamps.

Conclusion and outlook

We developed a versatile thermal analysis based method for the characterization of elemental sulfur, especially for the speciation of its vapor. The Skimmer coupling enables the online characterization of low volatile compounds in the vapor phase. It is an alternative method to KEMS, which is rarely available, and is even more rare with soft ionization.

The described method applies an easy to handle, commercially available lamp for the production of ionizing photons, there is no need for synchrotron or monochromator in contrast to older KEMS devices. Photoionization of the species enables the fragment-free characterization of the evolving species. The direction of further development is to use more intense photon sources, since enhanced photon densities (as showed in the case of EBEL vs. deuterium lamp) will lead to even smaller limits of detections.

We detected the species S_n (n=2-8) in sulfur vapor. The measured vapor compositions have to be corrected with the cross sections of the respective species to get more exact relative quantification. To achieve that, quantum chemical calculations will be done. The spectra of the used lamps were recorded, for future cross section calculations. The high potential of the approach implies further elucidation of allotrope forming elements such as selenium, tellurium etc. with higher boiling points.

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