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Laser ablation synthesis and TOF mass spectrometric identification of tellurium, sulfur and mixed tellurium–sulfur clusters

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Abstract

It was found that laser ablation of a mixture of elemental tellurium and sulfur is a possible way for synthesis of heteroatomic clusters. Four new cluster families with the composition $TeS_n (n = 1–14)$, $Te_2S_n (n = 1–10)$, $Te_3S_n (n = 1–6)$ and $Te_4S_n (n = 1–2)$ were produced with a negative or positive charge. Simultaneously, the formation of Te_n^+ and $Te_n^- (n = 1–6)$, $S_n^+ (n = 1–11)$ and $S_n^- (n = 1–15)$ clusters was observed. Isotopic patterns of the clusters mass spectra were found to be in a good agreement with theoretical models calculated from natural abundance of tellurium and sulfur isotopes. However, in spite of a high resolution achieved (4000), some mixed clusters are difficult to distinguish, because Te_mS_n cluster ions yield almost the same molecular weights and isotopic patterns as $Te_{m-1}S_{n+4}$ ones.

Keywords: Tellurium; Sulfur; Clusters; Laser ablation synthesis; Mass spectrometry; Post-source decay

1. Introduction

Laser ablation is one of the most prospective methods for the preparation of thin films. It was found that the structure of the deposited film depends on the nature of clusters produced by the laser ablation process [1]. As the clusters are also induced in ionised form, mass spectrometry is a powerful tool for their identification. The performance of mass spectrometry can be enhanced when elements with more isotopes are studied, e.g. tellurium [2]. However, the resolution of the spectrometer must be sufficiently high to enable the observation of isotopic patterns of the peaks.

The formation of tellurium clusters has been achieved using several different methods. Tellurium clusters in the size range of 2–20 atoms can be produced by laser vaporisation in pulsed-nozzle molecular beam source. Cluster distributions were characterised by direct sampling of cations condensed from the vaporisation plasma and by photoionisation of neutral species [3]. The formation of Te_n clusters ($n = 2–9$) has been studied in a supersonic molecular beam and their structures were investigated using vacuum UV–photoelectron spectroscopy and photoionisation—time of flight mass spectrometry [4]. It was also observed that tellurium clusters grow under the presence of metal impurities [5]. For example, traces of dysprosium facilitate the formation of Te_nDy clusters ($n = 5–25$) but also the effect of helium gas pressure was found to be important. In the presence of nickel and copper, laser ablation leads to the formation of binary ions $CuTe_n^+$ and $NiTe_n^+$ with $n = 1–8$ [6]. It was found that tellurium clusters are stabilised in large cavities of zeolite A [7]. Especially, tellurium is stabilised in the form of Te_8 rings. The possible reason for this stability is a good compatibility of the size and symmetry of either Se_{12} or Te_8 with the size and symmetry of large zeolite A cavities. Compounds containing homopolyatomic cluster cations of Te_n^{2+} ($n = 4$, 6–8, 10) can also be synthesised by the vapor transport reaction of tellurium with transition metal halides or oxohalides at a temperature of 100–300 °C with the reaction time of several days or weeks [8].

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In the case of interaction between sulfur and tellurium, we found only two papers focused on the neutron scattering study of alloys, which studied the miscibility gap occurring when sulfur and tellurium are present in a molar ratio of 4–6 [9,10]. The limiting factor for such studies may be the different volatility of the elements, as the melting point of tellurium (449.5 °C) is higher than the boiling point of sulfur (446.7 °C). We found also a theoretical study of the mixed sulfur–tellurium cluster $Te_4S_4^{2+}$ based on density functional theory [11]. The molecular and crystal structure of the cation Te_6^{4+} and the heteroatomic cluster cation $Te_3S_3^{2+}$ were determined using X-ray diffraction and by means of ^{125}Te nuclear magnetic resonance [12,13].

In previous works [6,14], the formation of elemental tellurium and sulfur clusters has been reported. As in these works the resolution of used mass spectrometers was rather low (we estimate that it could be close to just 150), the isotopic patterns of the peaks were not observed and it leads to uncertainty in spectra interpretation.

Because mixed Te–S clusters are described only in crystal structures, in this work the possibility of laser ablation synthesis and analysis of tellurium, sulfur and mixed tellurium–sulfur clusters is studied. Using a much higher resolution mass spectrometer, isotopic pattern measurement and modelling might enhance mass spectra analysis.

2. Experimental

2.1. Chemicals and reagents

Elemental tellurium (purity ≥99.999%) was purchased from Fluka (Buchs, Switzerland) and elemental sulfur from de Haën (Hannover, Germany). Suspensions were prepared in benzene from Lachema (Brno, Czech Republic). Bradykinin, α-cyano-4-hydroxycinnamic acid, guanosine-5′-monophosphate and harmane, all purchased from Sigma (Steinheim, Germany), were used as calibration standards for mass spectrometry. All these chemicals were of analytical grade purity, except of bradykinin, the purity of which was 98%.

2.2. Apparatus

Measurement of mass spectra was carried out on an AXIMA CFR (Kratos Analytical, Manchester, UK) mass spectrometer, equipped with a nitrogen laser wavelength of 337 nm. For the calibration of the positive mode, molecular ions $[M+H]^+$ of α-cyano-4-hydroxycinnamic acid and bradykinin were used. In case of the negative mode, $[M-H]^-$ ions of harmane and guanosine-5′-monophosphate were applied. Later, Te_n ($n = 2$–5) cluster peaks were used for the calibration of both modes. Each mass spectrometric analysis was performed using at least 100 shots and obtained data were accumulated.

2.3. Sample preparation

Because tellurium is not soluble in any solvent, suspensions of fine tellurium or sulfur powder in benzene (approximately 0.5 g ml^{-1}) in a volume of 1 µl were pipetted onto a sample plate and dried at room temperature. To prepare a mixture of fine powdered elemental tellurium and sulfur, the suspensions were thoroughly mixed in a vial with a glass stick.

3. Results and discussion

3.1. Te_n clusters

When applying laser power higher than 1.8 mW to a sample spot with elemental tellurium powder, the formation of Te_n clusters ($n = 2$–5) has been observed both in linear positive and negative modes, as well as in the reflectron modes. An example of a mass spectrum measured in the reflectron positive mode is given in Fig. 1. As could be seen in Fig. 2, isotopic patterns of the peaks are in agreement with theoretical models calculated according to the natural abundance of tellurium isotopes. Applying higher laser power (4 mW) resulted also in the formation of singly and either positively or negatively charged Te and Te_6 ions, which are not observed at lower laser energies. All observed tellurium clusters did not yield any post-source decay, even when extremely high laser power was applied (up to 5 mW), which reflects their high stability in vacuum.

We also studied the possibilities of using matrix-assisted laser desorption–ionisation of tellurium clusters

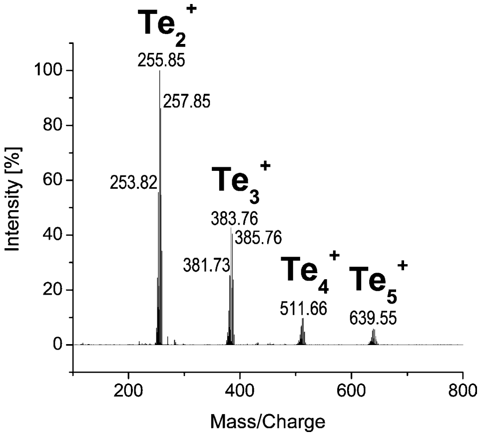

Fig. 1. Mass spectrum of tellurium clusters, produced during laser ablation of approximately 0.5 mg of fine tellurium powder, measured in reflectron positive mode with pulsed extraction and laser power of 2.67 mW.

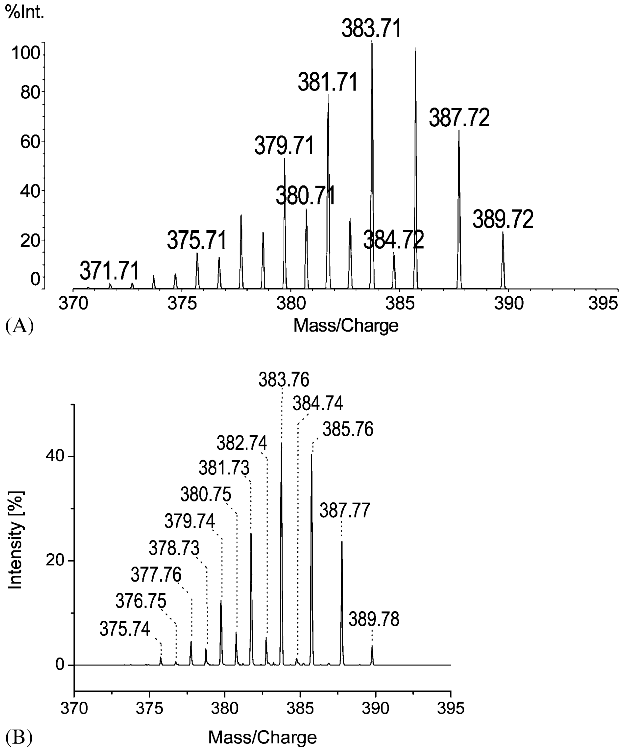

Fig. 2. Detail of Te_3^+ cluster mass spectrum (B), compared with theoretical isotopic distribution (A).

with several different matrices, such as α-cyano-4-hydroxycinnamic acid, ferulic acid, gentisic acid, 5-methoxysalycilyc acid, dithranol, 3-hydroxypicolinic acid and 2-(4′-hydroxybenzolazo)-benzoic acid. In their presence, we did not observe any enhancement of ionisation ability of tellurium clusters. Moreover, most of the matrices suppress the ionisation of Te_2 and Te_3 clusters. With similar results we also examined two possible novel matrices—diamond powder and fullerene C_{60}.

3.2. S_n clusters

Similarly to tellurium, via laser ablation of elemental sulfur powder, S_n clusters can be detected both in positive ($n = 3$–11) and negative mode ($n = 3$–15) after exceeding a laser power of 1.8 mW. As an example, a mass spectrum in the linear negative mode is shown in Fig. 3. Increasing laser power above 2.5 mW leads also to the formation of singly charged S_1 and S_2 clusters. After applying laser power higher than 3 mW, intense S_{n-1} and S_{n-2} charged fragments occur both in positive and negative PSD spectra. On the contrary, Te_n clusters, once formed, show extremely high stability and they are not decomposed in the PSD mode.

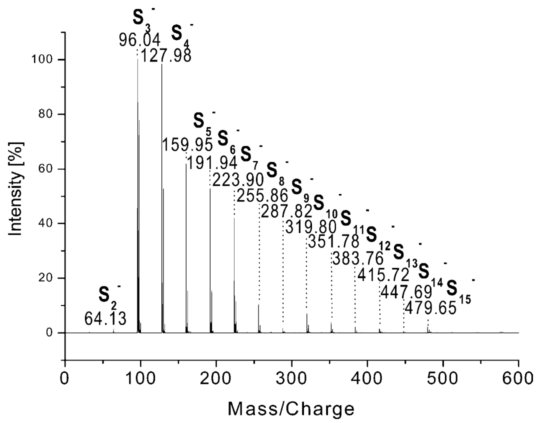

Fig. 3. Mass spectrum of sulfur clusters, produced during laser ablation of approximately 0.5 mg of fine sulfur powder, measured in linear negative mode with pulsed extraction and laser power of 3.17 mW.

3.3. Mixed Te_mS_n clusters

To produce composite Te_xS_y clusters, a fine powdered mixture of elemental tellurium and sulfur was prepared. The formation of charged Te_xS_y clusters was observed only in a few ‘sweet spots’, probably in regions where the elements were in contact. The best results were obtained when tellurium and sulfur were mixed in a molar ratio of approximately 1:2.5 (Te:S). The formation of mixed clusters of the same molecular weights was observed in linear positive, negative and also in the reflectron modes. An example of a mass spectrum showing the peaks of different mixed clusters can be seen in Fig. 4. Probable stoichiometry of mixed clusters is proposed in Table 1.

As the molecular weight of ^{128}Te-isotope (127.90446) is nearly the same as the sum of four atoms of ^{32}S (127.88828), the stoichiometry of the clusters cannot be determined from their molecular weights. From the comparison between the isotopic pattern and theoretical isotopic distributions, which is given in Fig. 5, it is possible to suppose that a mixture of more different clusters of the same molecular weight is formed and

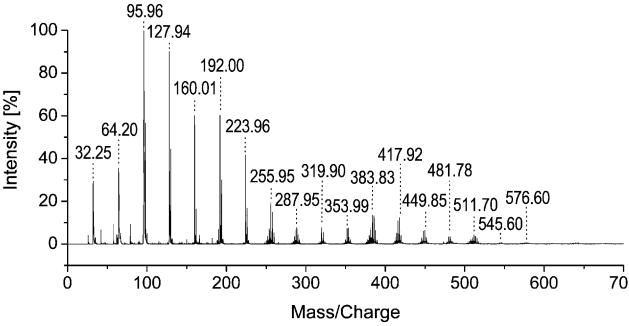

Fig. 4. Mass spectrum obtained from laser ablation of approximately 0.5 mg of a mixture of elemental tellurium and sulfur (in molar ratio 1:2.5), measured in linear negative mode with pulsed extraction and laser power of 2.83 mW.

Table 1
Mixed tellurium–sulfur cluster ion molecular weights and proposed stoichiometries

Mass/charge	Possible stoichiometry of the clusters
32.25	S^-
64.20	S_2^-
95.96	S_3^-
127.94	S_4^-, Te^-
160.01	S_5^-, TeS^-
192.00	S_6^-, TeS_2^-
223.96	S_7^-, TeS_3^-
255.95	S_8^-, TeS_4^-, Te_2^-
287.95	S_9^-, TeS_5^-, Te_2S^-
319.90	S_{10}^-, TeS_6^-, $Te_2S_2^-$
353.99	S_{11}^-, TeS_7^-, $Te_2S_3^-$
383.83	S_{12}^-, TeS_8^-, $Te_2S_4^-$, Te_3^-
417.92	S_{13}^-, TeS_9^-, $Te_2S_5^-$, Te_3S^-
449.85	S_{14}^-, TeS_{10}^-, $Te_2S_6^-$, $Te_3S_2^-$
481.78	S_{15}^-, TeS_{11}^-, $Te_2S_7^-$, $Te_3S_3^-$
511.70	S_{16}^-, TeS_{12}^-, $Te_2S_8^-$, $Te_3S_4^-$, Te_4^-
546.60	S_{17}^-, TeS_{13}^-, $Te_2S_9^-$, $Te_3S_5^-$, Te_4S^-
576.60	S_{18}^-, TeS_{14}^-, $Te_2S_{10}^-$, $Te_3S_6^-$, $Te_4S_2^-$

ionised. This conclusion is supported by the fact that the isotopic distribution of the peaks is not in a complete agreement with any of the models. Post-source decay analysis with the ion gate set to 405–430 Da resulted in the formation of S_{12}^- and S_{11}^- ions. This observation additionally complicates the interpretation of that selected cluster spectrum, which at first look seems to be a mixture of TeS_9 and Te_2S_5. The results of PSD analysis unambiguously reflect to the presence of S_{13}^-, which must, however, also take part in the isotopic pattern of the peaks. Therefore, it is not possible to expel the presence of any of the four proposed clusters. In other words, S_{13}, TeS_9^-, $Te_2S_5^-$, Te_3S^- are not distinguishable and most probably all of them are formed simultaneously.

We met with the same problem when trying to determine the structure of all other composite clusters, where none of them was in complete agreement with the model and yielded PSD reflecting to the presence of a S_n cluster. Unambiguous interpretation of the spectra would be possible with a mass spectrometer of resolution at least 50 000.

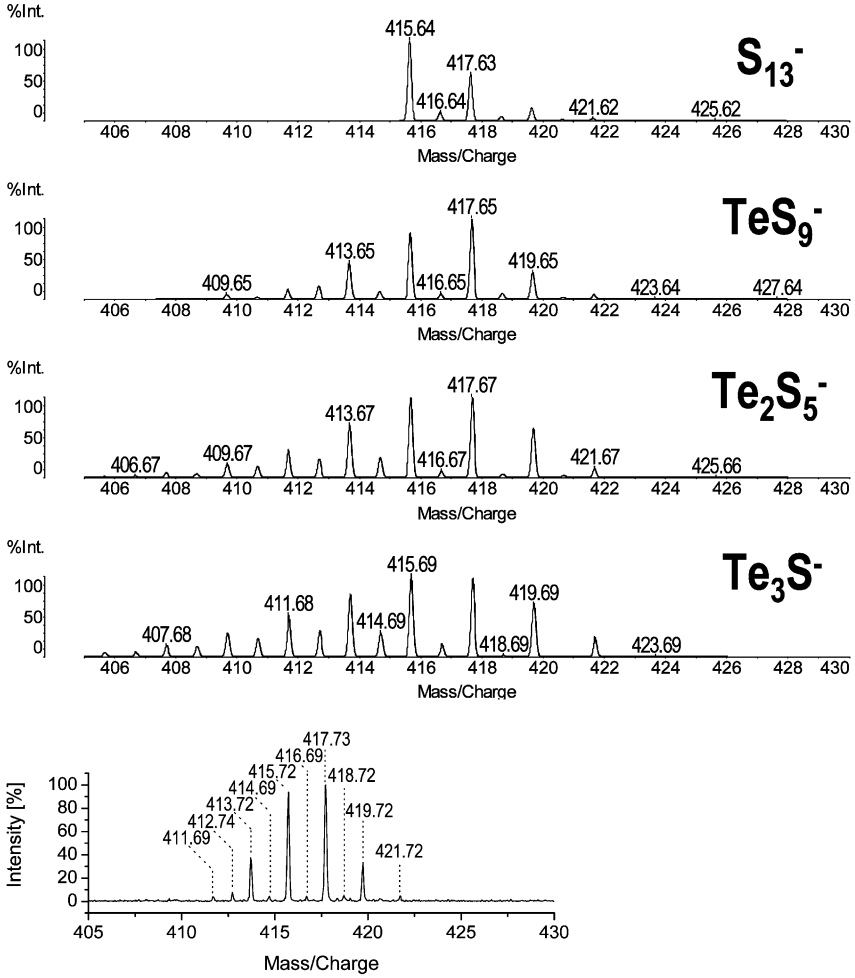

Fig. 5. Detailed look on a mass spectrum of mixed Te_nS_m clusters around $m/z \approx 417.7$, measured in reflectron negative mode with pulsed extraction and laser power of 3.5 mW (at the bottom). Comparison with isotopic patterns of S_{13}, TeS_9, Te_2S_5 and Te_3S.

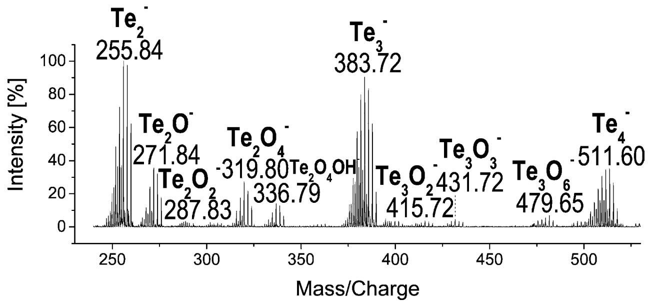

Fig. 6. Mass spectrum of tellurium clusters, produced during laser ablation of approximately 0.5 mg of fine tellurium powder, measured in linear negative mode with pulsed extraction and laser power of 2.67 mW.

3.4. Detection of tellurium oxides and hydroxo-oxides

It is interesting to note that in the linear negative mode via laser ablation of metallic tellurium, beside the formation of Te_n^- clusters, several weaker signals interpreted as tellurium oxides were observed. The mass spectrum together with proposed molecular formulas is given in Fig. 6. The formation of tellurium oxide and dioxide dimers and trimers was observed in agreement with the literature [15]. In addition, other different clusters were formed. We suppose that laser pulses induce the synthesis of all these species. After increasing the time of flight using the reflectron mode, oxygenated species were not observed, which reflects their relatively lower stability. From comparison of Figs. 4 and 6 it is evident that the presence of sulfur in the ablated mixture suppresses the creation of tellurium oxides, probably via formation of sulfur dioxide.

4. Conclusions

It was found that via laser ablation the synthesis of mixed Te_mS_n clusters is possible. The formation of singly charged tellurium and sulfur clusters was observed and, furthermore, confirmed using isotopic pattern modelling. Sulfur clusters are less stable than tellurium ones, as the former ones yield intense post-source decay. The formation of a family of new mixed $Te_xS_y^+$ and $Te_xS_y^-$ clusters with molecular weights up to 576.6 Da was observed. Because the atomic weight of ^{128}Te is almost the same as $^{32}S_4$, the composition of the mixed clusters is difficult to determine. In spite of this, it was possible to prove that mixtures of different clusters with equal molecular weights were ionised. Clusters $TeS_x (x = 1–14)$, $Te_2S_x (x = 1–10)$, $Te_3S_x (x = 1–6)$ and $Te_4S_x (x = 1–2)$ are formed simultaneously. Laser ablation of tellurium powder in the linear negative mode proves also the formation of tellurium oxides and hydroxo-oxides (Te_2O^-, $Te_2O_2^-$, $Te_2O_4^-$, $Te_2O_4OH^-$, $Te_3O_2^-$, $Te_3O_3^-$ and $Te_3O_6^-$).

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