Identification of molecules in graphite furnace by laser ionization time-of-flight mass spectrometry: sulfur and chlorine containing compounds

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An electrothermal vaporizer (ETV) coupled to a time-of-flight mass spectrometer (TOF-MS) with laser ionization (LI) was applied to the identification of molecules from sulfur and chlorine matrices in the furnace. An interface was developed to entrain furnace vapors from the matrices under study, *i.e.*, sulfur, sulfuric acid, magnesium sulfate, chlorides of sodium, potassium, caesium, magnesium, calcium and strontium, into the TOF-MS. These were then ionized on the TOF axis with 219, 240 and 266 nm laser radiations. The S^+ and SO^+ ions were mainly detected from sulfuric acid and magnesium sulfate in the furnace when ionized with a 219 nm beam. SO_2^+ was observed with 266 nm. Mainly S^+ and S_2^+ were detected when sulfur was ionized with 219 and 266 nm.

The spectra obtained at 219 nm were identical to those attained at 240 nm for the chloride matrices. The MCl^+, M_2Cl^+, M^+, and M_2^+ (where M is the metal) were observed for Na, K and Cs. Various compositions of oxides $(M_xO_y)^+$, M_2OCl^+ and chlorides MCl^+ and MCl_2^+ were identified for Ca and Sr. Mg only produced the Mg^+ isotopes.

1. Introduction

ETV with a continuous source of radiation and an ultraviolet (UV) multichannel detector spectrometer was employed recently for the systematic study of UV absorption spectra of inorganic compounds.[1–13] The setup was initially developed by Tittarelli *et al.*,[1–4] and later improved by Daminelli *et al.*[5–7] Investigations of alkaline earth fluorides and chlorides,[8–10] indium nitrate and Group 3 halides,[11] sulfides, sulfates and sulfur[12,13] were also carried out with this technique. The main objective of these studies was to identify species responsible for the absorption of the UV radiation. The gathered knowledge on the vapor phase composition of inorganic compounds can help with the optimization of experimental conditions, minimization of interference and improvement of analytical performance.[5] Spectral information is important for analytical applications of electrothermal atomic absorption spectrometry (ETAAS).

In all of the above studies except for sulfur compounds, the difficulties with identification of the broad bands that originate from the matrix were negligible due to availability of reference data. Problems were encountered, however, in the identification of the molecules that cause UV absorption in the case of sulfur matrices (Fig. 1). This work was coupled with the chlorides[5,10] to identify the species responsible for the broad nature of the bands that appeared in the early stages of the vaporization step.

TOF-MS coupled with a laser tuned to the wavelength of maximum UV absorption of the molecules was proposed to identify the absorbing species. In this study ETV was used to introduce the sample vapor into the ionization region of the TOF and provide identical thermal conditions to those used for UV absorption measurements obtained earlier.[6,7,10,12,13] Sample presentation by ETV has been reported to have many advantages (like slurry and solid introduction) over solution nebulization,[14] and the transport efficiency of the ETV was reported to be 20–80%, which allowed even smaller volumes to be used when liquids are employed.

Watson[15] used LI-TOF-MS as a tool for molecular weight determination and structural characterization of a variety of molecules, *e.g.*, the mono-metallic complex [Ir(dpp)Cl$_2$](PF$_6$), that illustrated the capability of the technique to identify molecules of high mass. Boesl *et al.*[16] showed that the technique provides for controlled fragmentation in the ion source, species selective ionization, high transmission and high resolution. Choi *et al.*[17] studied the multiphoton ionization and dissociation dynamics of methyl iodide clusters when 266 and 355 nm ionization and a reflectron TOF-MS were used. They detected CH_3^+, I^+ and I_2^+ fragments at 266 nm, and considerable amounts of parent ion (CH_3I^+) and methyl rich fragments (($CH_3I)_nCH_3^+$, where n is <9) at 355 nm.

The current study presents the mass spectra of positive ions obtained when sulfur, sulfuric acid, magnesium sulfate, chlorides of sodium, potassium, caesium, magnesium, calcium and strontium were vaporized in the graphite furnace. The vapors
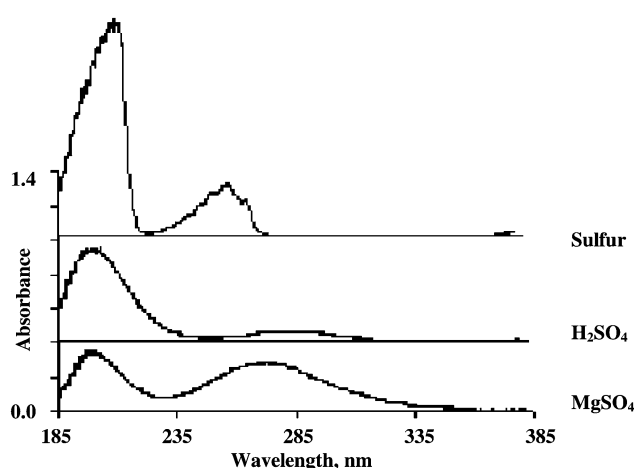

Fig. 1 UV absorption spectra of MgSO$_4$, H$_2$SO$_4$ and sulfur powder.

Table 1 The fast thermal program used for the vaporization of compounds

Stages[a]	Temperature/°C	Ramp or Hold/s	Flow rate/L min^{-1}
1	150	10 R	0.5
2	170	80 R	0.5
3	170	30 H	0.5
4	250	10 R	0.5
5	2200	1 R	1.0
6	2200	6 H	1.0

[a] Data acquisition stages are 5 and 6.

were entrained into the ionization chamber of a TOF-MS and ionized by a laser tuned to the wavelengths of maximum UV absorption. The purpose of this study was to use LI with TOF-MS for the identification of the molecules that caused the absorption spectra of the matrices already observed by vapor-phase UV spectrometry.

2. Experimental

2.1. Graphite furnace vaporizer

Vaporization was carried out with a Shimadzu GFA-4A graphite furnace atomizer. The furnace assembly was fitted with a Varian type pyrocoated tube and purged with either 0.5 or 1.0 L min^{-1} of 99.999% pure He (supplied by Air Products) or Ar (supplied by Air Liquide) gas. During the vaporization step that lasted 7 s for the fast thermal program (Table 1), the furnace was set either to heat from 250 to 2200 °C at maximum heating rate, which resulted in a time of 2 s to reach the upper temperature, or 6 s with a slower ramp (Table 2). The choice of a fast program in Table 1 was to work under the thermal conditions close to those employed for the already acquired UV absorption spectra. The slow program was used for the chlorides because their spectra appeared early (low temperatures) when a fast program was used. Tube temperatures were measured with a Mikron M90H pyrometer.

Table 2 The slow thermal program used for the vaporization of compounds

Stages[a]	Temperature/°C	Ramp or Hold/s	Flow rate/L min^{-1}
1	150	10 R	0.5
2	170	80 R	0.5
3	170	30 H	0.5
4	250	10 R	0.5
5	2200	6 R	1.0
6	2200	1 H	1.0

[a] Data acquisition stages are 5 and 6.

2.2. Tunable laser

Ionization of molecules was accomplished by laser radiation at 219, 240 and 266 nm. The choice of wavelengths followed the difficulty in the identification of molecules giving rise to the broad absorption observed by vapor-phase UV spectrometry. Moreover, these are the maximum peaks attainable by the Coumarin dyes used for wavelength tuning.

The 219 and 240 nm were generated by a dye laser (D-3400 Göttingen Lambda Physik) pumped with a 308 nm XeCl excimer laser (Lambda Physik EMG201 with an EMG 101 power supply) of ∼300 mJ to supply a beam of ∼20 mJ at 438 and 30 mJ at 480 nm, respectively. The Lambda Physik dye solutions used were prepared in methanol AR (from Associated Chemical Enterprises). A 0.084% LC 4400 (Coumarin 120) was used for 219 nm and 0.23% LC 4800 (Coumarin 102) for 240 nm. The 438 and 480 nm radiations were then frequency doubled by a beta barium borate (BBO) crystal to yield the UV beams of ∼1.5 and 2 mJ per pulse, respectively.

The 266 nm beam of 3 mJ output was obtained from a 1064 nm Nd:YAG laser (Model PL-9010, Continuum Corporation) that was frequency quadrupled using BBO crystals. These beams were sent unfocused or semi-focused through the ionization region of the TOF to ionize the molecules present. The unfocused beam resulted in a sample irradiation of ∼55 mJ cm^{-2} (*i.e.*, a power of 2.75 MW cm^{-2}). The semi-focused condition was achieved when a 200 mm focal length fused silica lens was used to focus the beam 50 mm beyond the ionization position (on the axis of the TOF). This led to an irradiation of 220 mJ cm^{-2} with a pulse duration of approximately 20 ns.

2.3. Reflectron type time-of-flight mass spectrometer

The locally made reflectron TOF-MS (Fig. 2(a)) with a suitable interface (Fig. 2(b)) was used to analyze sample vapors that emanated from the sample introduction hole of the heated graphite furnace. The vapors are entrained through a 0.5 mm aperture situated as near as possible to the sample introduction hole of the furnace but without contact, *via* an intermediate chamber pumped to a pressure of 1 Torr by a 60 m^3 hr^{-1} Alcatel mechanical pump, and then through a 0.6 mm skimmer into the ionization chamber. This is pumped by a 200 L s^{-1} turbomolecular pump (Pfeiffer Balzers TCP121) to a pressure of about 5 × 10^{-4} Torr. The ions created are accelerated by static electric fields into the flight tube, separated from the ionization chamber by a 3 mm aperture and pumped separately by another 200 L s^{-1} turbo pump to a pressure of <10^{-5} Torr. The reflectron configuration employed resulted in a mass resolution of about 500 ($m/\Delta m$) at low masses around m/z = 30. Such resolution, however, was not even nearly obtained during the measurements described here. Due to the transient nature of the signal, as well as the relatively low repetition rate
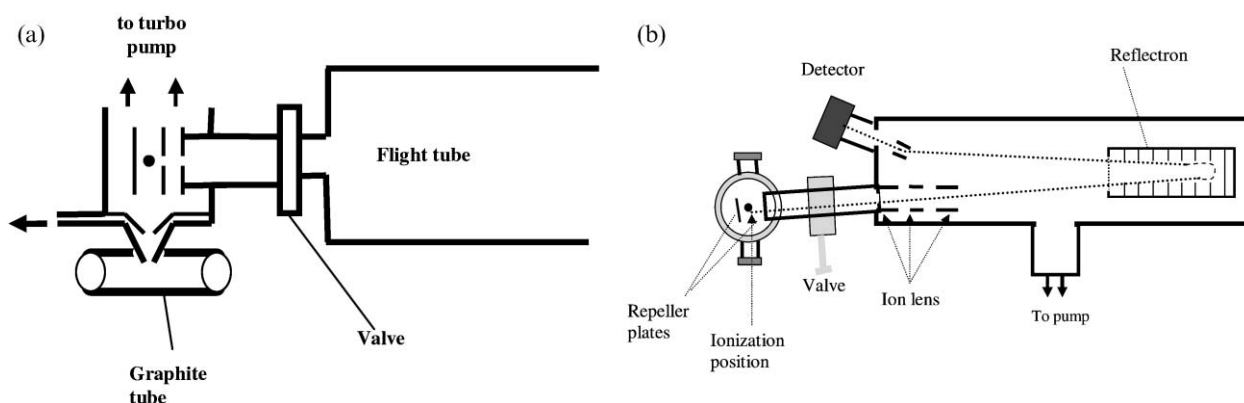

Fig. 2 (a) Electrothermal vaporizer coupled to a time of flight mass spectrometer. (b). Reflectron type time of flight mass spectrometer.

of the laser (10 Hz), the signals shown in the figures are always due to a single laser pulse. The signals of high intensity are severely broadened due to saturation in either the measurement system (amplifier and signal averager), the detector itself (single microchannel plate of 32 mm diameter from Burle Electro-Optics and electron multiplier R2362 from Hamamatsu), or space charge effects in the source region, where a high concentration of ions are created in a short time. Isotope ratios in the observed signals were seldom found to correspond to the natural ratios, due to the single laser event giving rise to the signal.

A transient signal averager (EG&G 9846) was employed to collect data during the vaporization step (record lengths between 2048 and 8192 points, sampling each 8, 16 or 32 ns with variable number of sweeps to average). This system does not average onboard, and the result of each sweep is transferred to the host computer, which resulted in a maximum of 10 Hz repetition rate.

2.4. Reagents and procedure

All reagents used were of analytical grade. An ultra pure water system (Millipore Microsep, South Africa) was employed to generate 18.2 $M\Omega$ cm resistivity deionized water. Aqueous solutions of H_2SO_4 from Associated Chemical Enterprises, $MgSO_4$ and NaCl from Saarchem, CsCl from Aldrich, $CaCl_2 \cdot 2H_2O$ from NT laboratories, KCl, $MgCl_2 \cdot 6H_2O$ and $SrCl_2 \cdot 6H_2O$ from Riedel-De Haën prepared at concentrations (0.1–1% metal) suitable for their molecular ion detection and small amounts of sulfur powder were employed.

About 20–40 µl of solution was manually pipetted into the graphite furnace which was then secured onto the skimmer and vaporized according to the thermal program reported in Tables 1 or 2. The vapors were entrained into the TOF ionization region, ionized by a semi-focused or unfocused 219, 240 or 266 nm laser beam. The mass spectra recorded were stored in the memory of the computer.

3. Results and discussion

Vaporization of H_2SO_4, $MgSO_4$, NaCl, KCl, CsCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot 6H_2O$ was carried out for 7 s according to the two thermal programs shown in Tables 1 and 2, for the fast and slow heating rates, respectively. A total of 24 spectra were collected for each experiment though each figure presents only the most intense spectrum. The two

thermal programs provided similar spectral features in spite of the different heating rates. The unfocused and semi-focused beams yielded similar results too, with only the intensities of the bands under semi-focused conditions being higher. In the experiments where the beam transmission was attenuated to 14 or 35%, the results showed only reduction in signal intensity in comparison with the 100% transmission, *i.e.*, there was no change in speciation of molecular ions with increase of laser power.[18] With Ar or He as carrier gas, again the mass spectra were almost identical. Since there was insignificant absorption at 240 nm for sulfur compounds, experiments at this wavelength were not carried out for these compounds.

This paper presents only the spectra obtained (1) when the fast thermal program was used, (2) with Ar as a carrier gas, (3) when a 100% transmitted semi-focused laser beam was applied, and (4) with wavelengths of 219 and 266 nm being used for H_2SO_4 and $MgSO_4$ while 240 nm was applied for NaCl, KCl, CsCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$ and $SrCl_2 \cdot 6H_2O$, since the chlorine containing compounds showed similar spectral features at all abovementioned wavelengths.

3.1. At 219 nm

The spectrum of $MgSO_4$ obtained when it was introduced as a 20 µl aliquot of 0.1% Mg solution in the furnace is presented in Fig. 3. Strong signals of SO^+ and S^+ were recorded; even the $^{34}S^+$ isotope contributions are evident. A peak at mass 40 was also observed and assigned to Ar^+.

The spectrum of 40 µl of 1% H_2SO_4 solution, shown in Fig. 4, is almost identical to that of $MgSO_4$, Fig. 3.

The spectrum obtained for S, introduced into the atomizer as the solid, is shown in Fig. 5. In addition to the SO^+ and S^+ signals, seen also in Fig. 3 and 4, a relatively strong peak at mass 64 is present. This can only be attributed to S_2^+, since SO_2^+ was never seen in any of the experiments above.

The interpretation of the spectra to identify the molecules responsible for the UV absorption is not straightforward, due to fragmentation of the molecules by the absorbed laser energy. When an SO_2 gas mixture (1000 ppm in nitrogen) was aspirated into the TOF-MS *via* the same path as the furnace vapors, the spectra with unfocused as well as semi-focused beams consisted of SO^+ and S^+ only. It was also established by photoacoustic measurements with the above mentioned mixture of SO_2 that it absorbs at the wavelength of 219 nm, and we thus conclude that the SO_2 molecule is almost completely fragmented to SO^+ and S^+, even by the unfocused beam. For $MgSO_4$ and H_2SO_4,
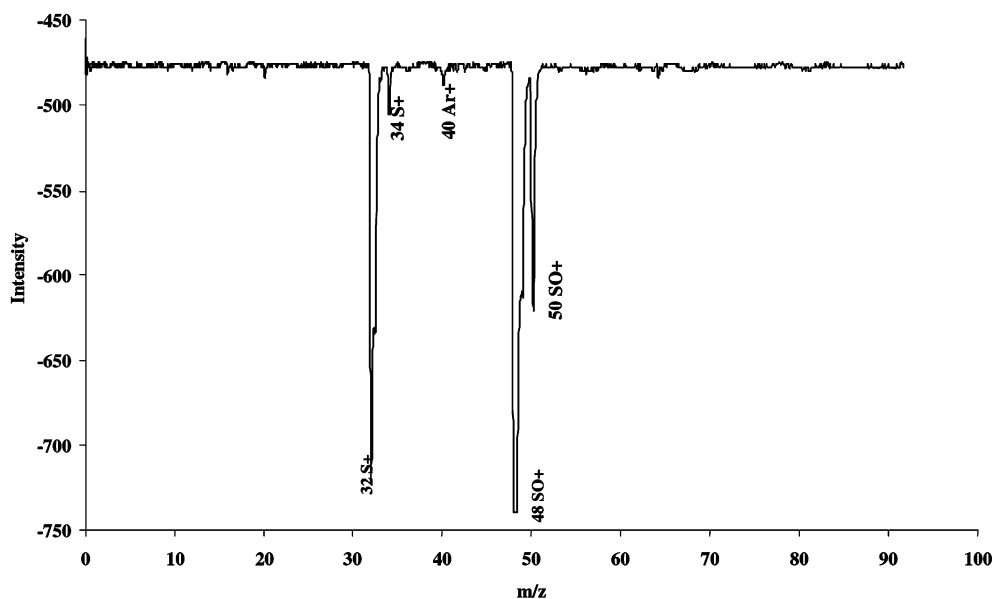

Fig. 3 $MgSO_4$ at 219 nm.

Fig. 4 H$_2$SO$_4$ at 219 nm.
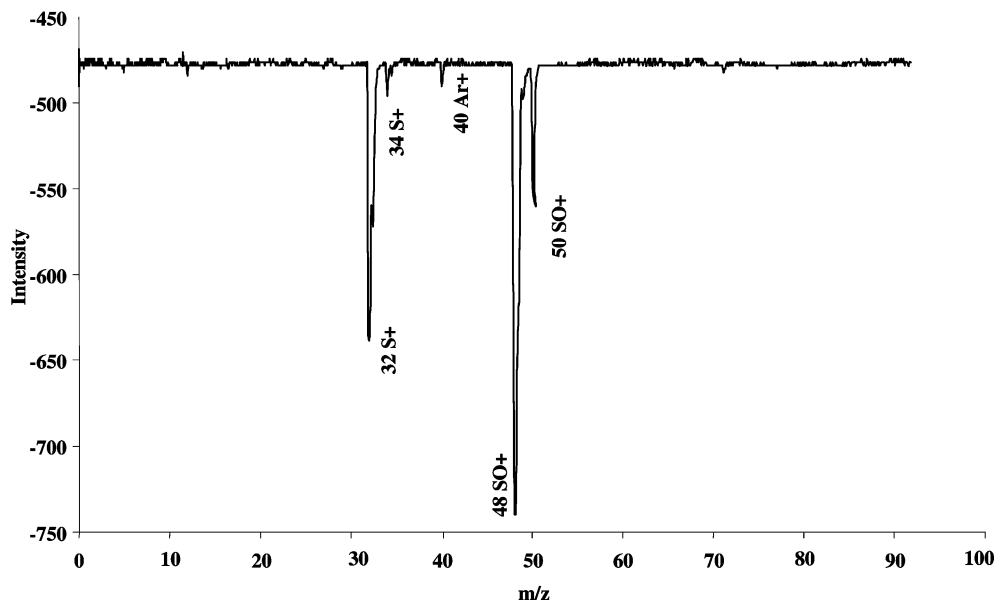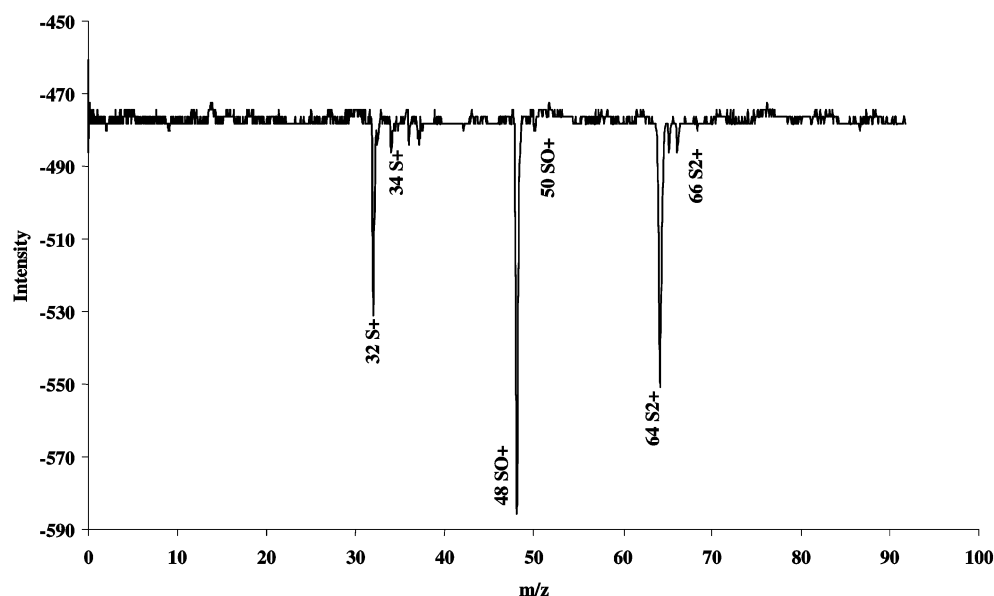

Fig. 5 Sulfur at 219 nm.

which provided similar spectral features, in terms of UV absorption (Fig. 1) as well as TOF mass spectra (Figs. 4 and 5), it can be concluded that the UV absorption in the furnace is caused by either one or both of the SO and SO$_2$ molecules. The assignment of the peak at mass 40 to Ar$^+$ rather than MgO$^+$ is encouraged by its absence when the carrier gas was changed from Ar to He. This does not, however, exclude the formation of MgO in the furnace.

In the case of pure sulfur in the furnace, the strong peak at mass 64 indicates the presence of S$_2$$^+$ in the furnace (in view of the fact that SO$_2$ will also be completely fragmented if present). The S$^+$ observed is due to laser fragmentation of SO and/or SO$_2$, since the S atom does not absorb at this wavelength and will not be ionized. The stronger SO$^+$ peak, however, can only be attributed to the presence of this radical or, more likely, due to laser fragmentation of SO$_2$ formed in the furnace. The source of oxygen probably is due to memory effects from previous measurements.

It is also possible that larger clusters of sulfur existed which were responsible for the formation of S$^+$ and S$_2$$^+$ through fragmentation. Hearly et al.[18] identified cationic sulfur by laser ablation and obtained a positive ion spectrum which showed a greater range of sulfur species from S$^+$ to S$_{11}$$^+$. Larger clusters were reported to have existed over a small range of low laser power while S$^+$ dominated at high laser powers.

3.2. At 240 nm

The spectrum of NaCl obtained when introduced as 20 μl of 0.1% Na solution in the furnace is presented in Fig. 6. The major product ions in the spectrum are Na$^+$, Na$_2$$^+$, Na$_2Cl^+$ and also NaO$^+$, NaCl$^+$ and Na$_3$Cl$_2$$^+$. The formation of NaCl$^+$ is indicative of direct ionization of the NaCl molecule. Na$^+$ can be presumed to be a fragment ion from the dissociative ionization of neutral NaCl whose ion photodissociates by additional photoabsorption. As was reported in the work by Choi et al,[17] who said that clusters may form during ionization of polyatomic compounds, the same can be assumed in this case. However, additional work needs to be carried out to investigate this in detail.

The results obtained for KCl when 20 μl of 0.1% K was vaporized and ionized are presented in Fig. 7. Only K$^+$, K$_2$$^+$ and K$_2$Cl$^+$, species that have the same stoichiometric ratios as the most intense obtained with sodium chloride, were observed.
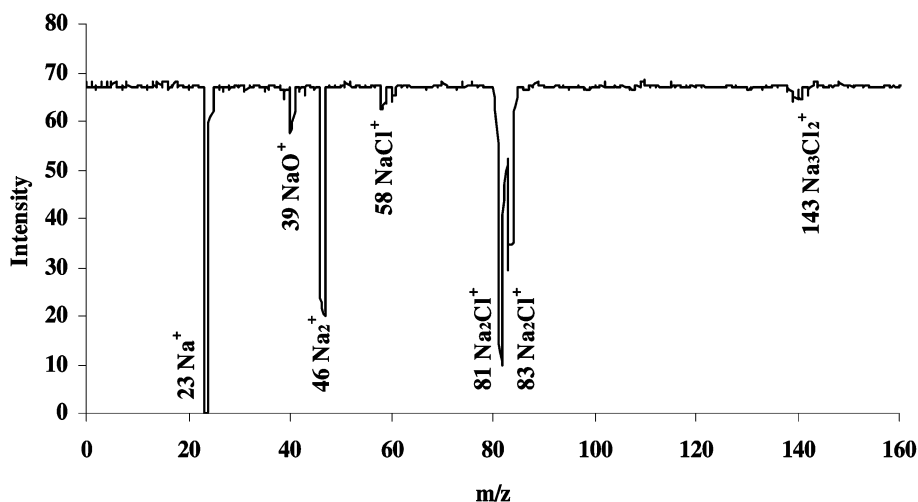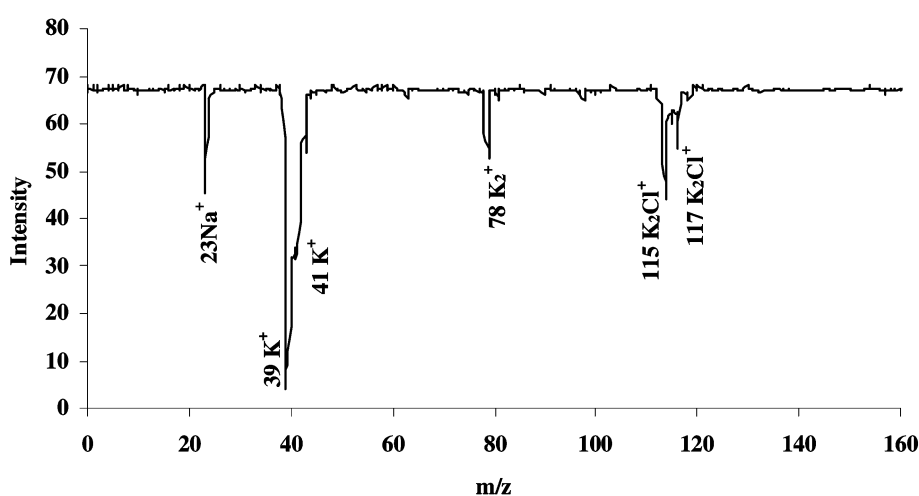
Fig. 6 NaCl at 219 nm.

Fig. 7 KCl at 219 nm.

In this case, the absence of the parent ion (KCl^+) can only mean that the laser energy achieved for this study was insufficient for ionization of KCl.

When CsCl was vaporized as 20 μl of 0.1% Cs and ionized, Cs^+ and Cs_2O^+ ions were detected. The results exhibit a high degree of hydrolysis undergone by CsCl in comparison with KCl and NaCl. This aspect can be associated with the less intense UV absorption spectra that resulted when CsCl was vaporized.[6]

A study on the ionization and dissociation processes needs to be carried out to identify the origin of element rich molecular ions, *e.g.*, Na_2Cl^+, K_2Cl^+, *etc.*

The $MgCl_2\cdot6H_2O$ spectrum is also not included due to its less detailed spectrum. Only the Mg^+ isotopes 24 and 25 were detected. It was reported earlier[7,10] that the position of maximum absorption by a band below 250 nm attributed to $MgCl_2$ shifted as the temperature increased. This indicated the presence of other species evolved together with the dichloride. The authors attribute this effect to partial hydrolysis undergone by $MgCl_2\cdot6H_2O$. It is appropriate to relate the responsible compound for absorption at 240 nm to MgO rather than $MgCl_2$, which fragmented into Mg^+. The presence of MgO was proposed by Katskov *et al.*[8] after the same spectral feature was observed for $Mg(NO_3)_2\cdot6H_2O$ and $MgCl_2\cdot6H_2O$.

The spectral features of $CaCl_2\cdot2H_2O$ and $SrCl_2\cdot6H_2O$ will be treated together since they are not so different. Oxides, sub-oxides, oxychlorides, mono-chlorides and Ca atomic isotopes were featured in the spectrum of 20 μl of 0.1% Ca as $CaCl_2\cdot2H_2O$ shown in Fig. 8.

In the case of $SrCl_2\cdot6H_2O$, whose spectrum is shown in Fig. 9, Sr atomic isotopes, mono-oxide, sub-oxide, mono- and dichlorides were observed. The detection of mixtures of chlorides and oxides, which is unique only to these compounds, is in line with the conclusion brought forward[9] about the decreased tendency of hydrolysis down the Periodic Table. The other factor is related to the high intensity of the broad band attributed to the dichlorides of these elements. Therefore, the responsible species for UV absorption can either be the dichlorides or oxides that lead to fragmentation, as seen in the respective spectra (Figs. 8 and 9).

3.3. At 266 nm

$MgSO_4$ and H_2SO_4 solutions produced similar spectra at 266 nm, an example of which is shown in Fig. 10 for $MgSO_4$. In these cases, in addition to the strong SO^+ and S^+ peaks, clear peaks at mass 64 were observed. This is ascribed to SO_2^+. The lower energy per photon, as well as the decreased UV absorption at this wavelength in comparison with that at 219 nm, leads to less fragmentation of the molecule. The UV absorption is presumed to have been mostly due to SO_2, which in this case fragmented into SO^+, S^+ and neutral O and O_2 which are lost.[19] In addition, laser fragmentation of parent molecules, *e.g.*, SO_2, can lead to the complete absence of these molecules in a spectrum, as was seen for SO_2 gas at the power densities used in this study. An earlier report[20] stated that one of the difficulties with the nanosecond regime was the absorption of one or more photons during the
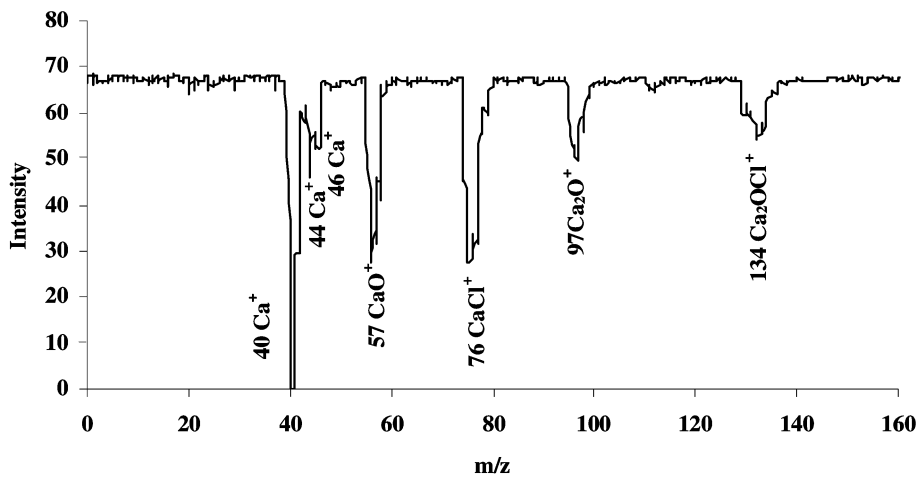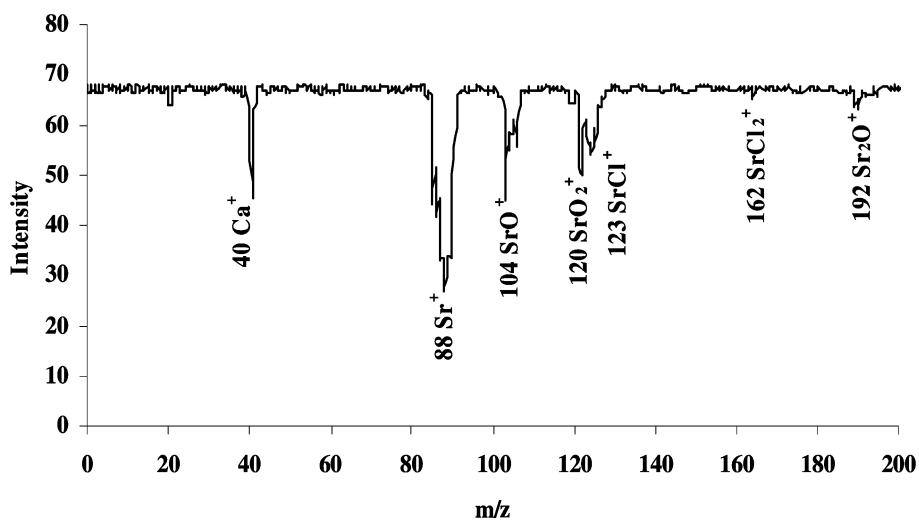
Fig. 8 $CaCl_2 \cdot 2H_2O$ at 240 nm.

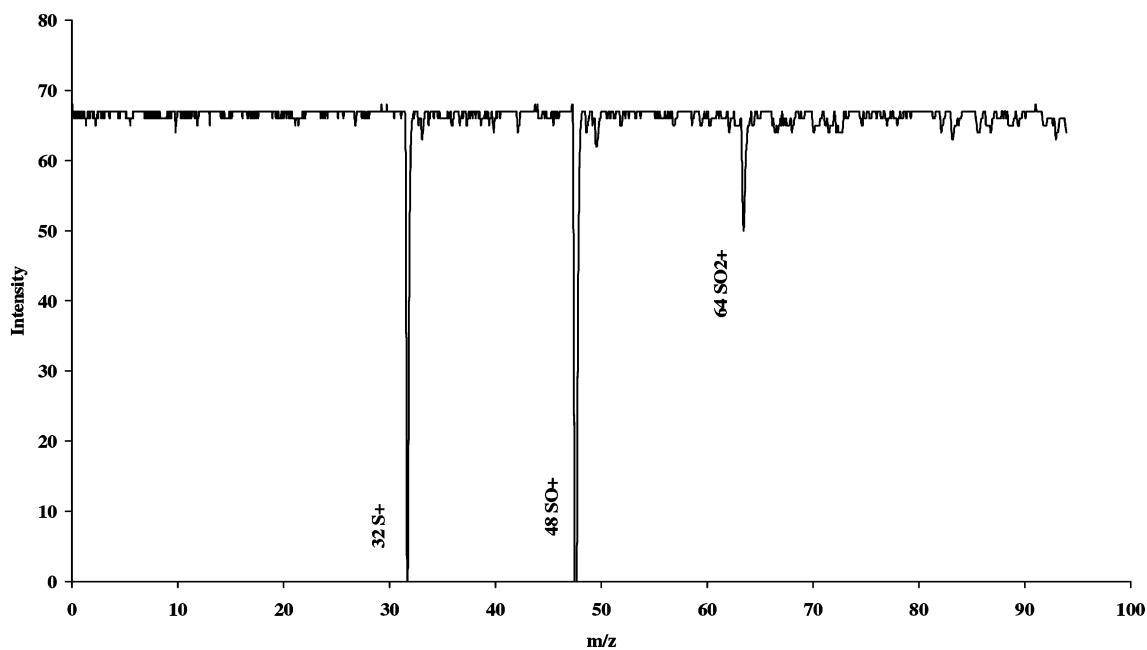
Fig. 9 $SrCl_2 \cdot 6H_2O$ at 240 nm.

Fig. 10 $MgSO_4$ at 266 nm.

detection of molecular species that might reach dissociative states below ionization limit, which can cause the production of neutral species. This would lead to small or even no parent ion

(*e.g.*, $MgSO_4^+$ or $H_2SO_4^+$) detection and hence ambiguous analysis.

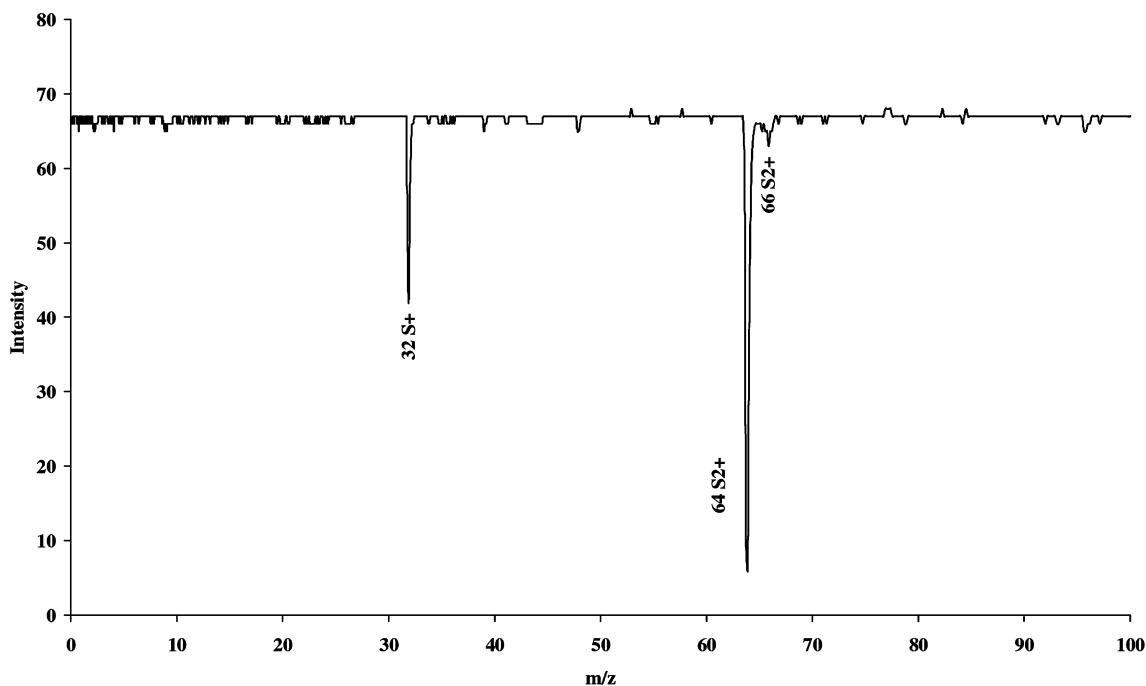The solution can be: (1) the use of high flux (10^{26} photons per

Fig. 11 Sulfur at 266 nm.

second) femtosecond lasers to initiate the multiphoton absorption within femtosecond pulse duration to efficiently ionize with considerable less fragmentation of parent molecules;[19] (2) the use of hybrid instruments like the quadrupole-TOF, an MS/MS[21] technique employed to obtain structure information about molecules. A quadrupole here would be used to select a certain mass of a parent ion whose formula is that of the original matrix introduced into the graphite furnace. By collisions with gas molecules in a small cell, the parent ion will break up into daughter ions which will then be detected by TOF-MS.

The mass spectrum obtained with pure S in the furnace is shown in Fig. 11. In this case the 64 peak is the strongest, with the only other prominent peak at mass 32 of approximately half the intensity. Based on this and the absence of SO^+ peak, it can be concluded that the larger sulfur cluster, namely S_4, is responsible for the absorption feature in the vicinity of 266 nm, as shown on the UV spectrum of sulfur in Fig. 1.

4. Conclusions

It was shown in this work that LI-TOF-MS could be used to assist with the identification of the molecules responsible for the UV absorption spectra observed from sulfur and chlorine containing matrices. It can also be useful to study chemical and physical processes that are impossible to detect with UV absorption spectrometry. The method is believed to be applicable to many other known matrices.

The problems experienced with the present method of ionization are the dissociation of the original molecule prior to ionization and laser fragmentation of the original molecule which makes it difficult to identify the parent species. These need to be further studied in detail. Longer wavelengths (IR) should be employed to test if fragmentation will be minimized as reported.[22]

The method may be useful in conjunction with UV absorption spectrometry in the frame of compilation of a reference atlas of vapors of inorganic compounds present in the furnace.

Acknowledgements

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