

Threshold ionisation mass spectrometry (TIMS); a complementary quantitative technique to conventional mass resolved mass spectrometry



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ABSTRACT

The mass analysis of gas mixtures using quadrupole mass spectrometers is a well developed analytical technique which is routinely used with great success. The spectrometer's ionisation source is commonly one in which electrons from a heated filament are accelerated to around 70 eV before impacting with the gas samples. There are significant advantages, however, in being able to use other electron energies. Lower energies are particularly useful and are used in a so-called Threshold Ionisation mass spectrometry (TIMS) mode. The work described here applies the TIMS technique to a variety of problems which historically have proved to be difficult, and in some cases intractable, using the conventional mass resolved mode of mass spectrometry. The problems tackled include $^4\text{He}/\text{D}_2$ and $^3\text{He}/\text{HD}$ separation in nuclear fusion research, measuring trace levels of NH_3 in air, and the separation of contributions from nitrogen and carbon monoxide to the QMS mass peak at $m/z = 28$. Finally, for measurements at higher gas pressures in the mass spectrometer, data for the production of long-lived metastable species are described.

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1. Introduction

The mass analysis of mixtures of gases using quadrupole mass spectrometers is a well developed analytical technique which is routinely used with great success. In its simplest form, the gases in the mixture are ionised in the spectrometer's ionisation source and the ions produced are mass-resolved as they travel through the quadrupole system before detection using either Faraday detectors, secondary electron or pulse-counting channeltron multipliers. The output display is a plot of the relative abundances of the positive ions as a function of their mass/charge ratio. The ionisation source is commonly one in which electrons from a heated filament are accelerated to around 70 eV before impacting with the gas samples introduced into the source. In the work to be described here, the pressure of the gas in the source will be from UHV up to the 10^{-3} – 10^{-4} Pa typical operating range of standard quadrupole mass spectrometer systems. Recently, QMS systems which allow use of

source pressures of up to 0.03 Pa have been developed, and are particularly well-suited for examining gas samples originating in plasma-processing systems. This current work presents such recent application data and is discussed below.

The selection of 70 eV for the energy of the electrons in the ionisation source is based on the fact that this energy is for many gases that which corresponds to the peak of the ionisation vs electron energy cross-section curve [1]. However, there are significant advantages in being able to use other electron energies, as provided for example, in gas analysis systems which allow the selected electron energy to be between 4 and 150 eV and to be varied in 0.1 eV steps. The lowest energies (≤ 24.5 eV) are particularly useful and are used in the so-called Threshold Ionisation (TIMS) mode.

TIMS is a well understood technique, with some of the first studies described by Fox et al. [2], and Fox and Hickham [3], who obtained ionisation probability curves for common species such as CO^+ , N_2^+ , C_3H_6^+ , and C_6H_6^+ from a monoenergetic electron impact source. TIMS is based on the fact that for all gases any ionisation process which produces a positive ion in a collision between a gas molecule and an energetic electron has a minimum threshold energy, with the threshold energy characteristic of the particular ionisation process. It follows that TIMS analysis can show relative ion abundance. Initial TIMS work on metastable states of N_2

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molecules was reported by Foner and Hudson [4], with later studies reported by Agarwal et al. [5]. More recently Pulpytel et al. [6] have applied TIMS to measure excited molecular oxygen states $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g)$ during plasma assisted chemical vapour deposition, which helped to characterise the electronic conductivity properties of the deposited thin films. In the following sections, applications of the TIMS technique to a variety of problems which have proved to be difficult to tackle using more conventional mass analysis are described, and demonstrate the complementary effectiveness of the technique.

2. Traces of organic and similar vapours in air

Fig. 1 shows a family of mass scans for a mixture of acetone and isopropyl alcohol in air for which the electron energy was increased from 10 to 13 eV. At these low energies, the electrons have insufficient energy to ionise the nitrogen in the air sample since the threshold energy for producing N_2^+ ions from N_2 is 15.7 eV and only shows small numbers of O_2^+ ions at energies above 12.2 eV, the threshold energy for O_2^+ ions from O_2 . The figure illustrates how TIMS may be used very effectively for studying traces of organic vapours and other similar substances with low threshold ionisation energies when present in other gases such as nitrogen whose ionisation threshold is a few eV higher.

3. Detection of ammonia in the presence of water vapour

A second example of practical interest in areas such as refrigeration, and the chemical industry is that of analysing ammonia in gas streams that have a high water vapour content. The spectral overlap between the $m/z = 17$ mass peak of both NH_3 and OH when the water vapour content of the gas stream is high makes it difficult to subtract the OH signal with adequate accuracy from standard conventional mass scans. However, as Fig. 2a and b illustrates, TIMS can provide a technique for species quantification.

Comparison of Fig. 2a and b shows that while the H_2O –Air sample shows no ionisation at energies below about 20 eV there is a significant signal for energies above about 13 eV when ammonia is added to the gas stream. Using an electron energy of 18 eV in the mass spectrometer ionisation source showed the detection limit to be better than 10 ppm of NH_3 in a 2% H_2O stream when using argon as the carrier gas. This is highlighted by the red line in Fig. 2a and b which clearly shows the generation of an ionisation signal at electron energies in the range 13–20 eV. At $m/z = 17$, this is due to the presence of NH_3^+ (Fig. 2b), as opposed to Fig. 2a where only

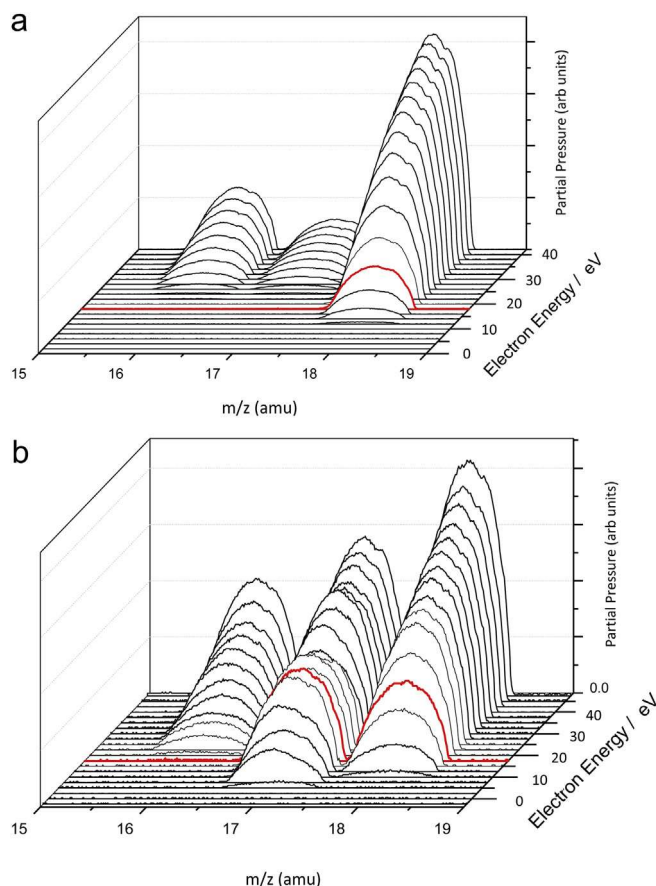


Fig. 2. a. (m/z vs electron energy for H_2O –Air), and b. (m/z vs electron energy for NH_3 – H_2O –Air mix). Note the x, y axes are the conventional m/z (amu) and partial pressure (arb units) respectively, with the z axis representing the variable electron energy (eV). The red line indicates the 18 eV electron energy threshold in the z plane.

OH^+ is present. This current work further illustrates the effectiveness of the TIMS technique by simultaneously varying the NH_3 concentration in a more complex gas mixture between 10 and 100 ppm, along with ppm levels of nitric oxide (NO) in 2% H_2O . The results are presented in Fig. 3 which show the mass spectrometer system scanning selected masses, as a function of time, at $m/z = 32$ (O_2), 18 (H_2O), 30 (NO) at the common 70 eV electron energy, with $m/z = 17$ (NH_3) at a reduced electron energy of <18 eV. The sharp

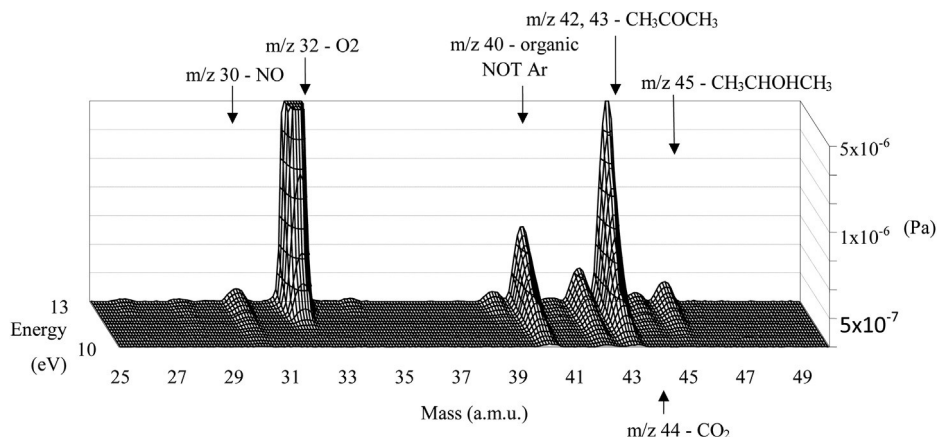


Fig. 1. Mass Spectrometric surface study of an Acetone/Isopropyl Alcohol/Air vapour stream at electron energies of 10–13 eV. The x, y axes are the conventional m/z (amu) and partial pressures units (Pa) respectively, with the z axis representing variable electron energy (eV).

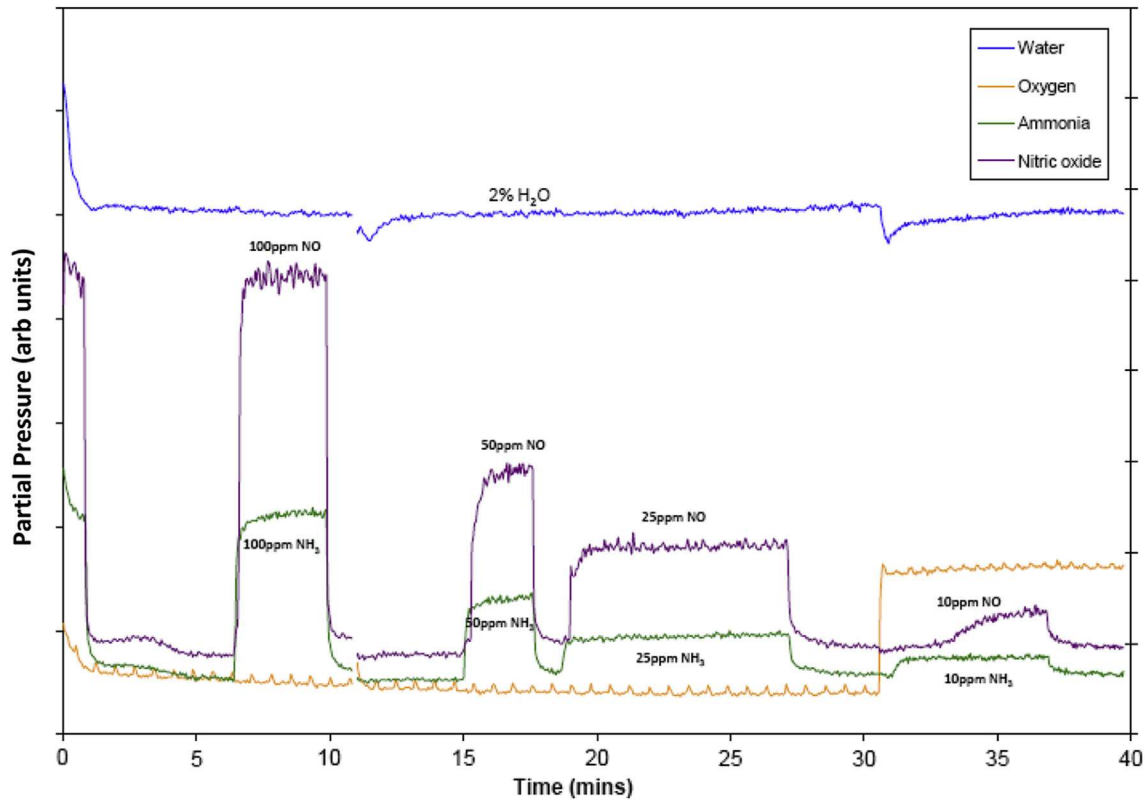


Fig. 3. Simultaneous measurement of low ppm levels of ammonia, nitric oxide and oxygen in percentage (2%) concentrations of water. TIMS at electron energy <18 eV used for NH_3 ppm detection at $m/z = 17$. Partial pressure (arb units).

increase in $m/z = 32$ (O_2) concentration at around 30 min, is simply a deliberate dosing of O_2 into the mixture to examine the effects on the NO concentration. This is ignored for the present discussion as it has no direct or indirect influence on the TIMS quantification of NH_3 . The data shows detection limits of better than 10 ppm NH_3 in water-rich gas are achievable with this complementary technique.

4. Mixed streams of deuterium and helium

In plasma fusion work, where helium ash is a by-product, the accurate determination of the helium/deuterium ratios is an important requirement. This quantification is normally precluded when using a small quadrupole mass spectrometer in conventional mass spectral mode due to the unresolvable mass overlap of both D_2 and He at $m/z = 4$, the actual mass separation being only 0.025 amu. When the two gases are present simultaneously, a typical electron energy spectrum for $m/z = 4$ is as shown in Fig. 4 for an example 1:1 mixture of D_2 :He. The onset of an ion signal at around 15.4 eV is due to production of deuterium ions and the sharp increase in the signal at around 24.5 eV is due to the onset of ionisation of the helium in the mixture. The ionisation threshold energies for D_2^+ from D_2 and He^+ from He are consistent with published data [7]. The TIMS spectrum shows a deconvolution of these two species. Applying rudimentary calculations to TIMS spectra such as that shown in Fig. 4, allows the presence of D_2 in Helium to be quantified to levels of <10 ppm.

In this current work, such a calculation to quantify the concentrations of D_2 and He from an unknown gas mixture is derived simply with application of the well established Bethe Encounter Binary (BEB) threshold ionisation cross section theory [1] to the TIMS spectral data. Considering the form of the TIMS spectrum, in Fig. 4, permits one to treat the continuous curve as two separate

regions, defined by either side of the inflection point, 24.5 eV, at which the ionisation of the deuterium transitions to the region which defines simultaneous ionisation of both deuterium and helium. The pre-transition region of the TIMS curve (<24.5 eV) can be reasonably approximated by the following expression:

$$N_{(\text{D}_2)} = A_i \left(\sigma_{(\text{D}_2)}^{(19 \text{ eV})} \right) \cdot \eta_{(\text{D}_2)} \quad (1)$$

Similarly, the post transition region of the curve (>24.5 eV), can be approximated by the following expression:

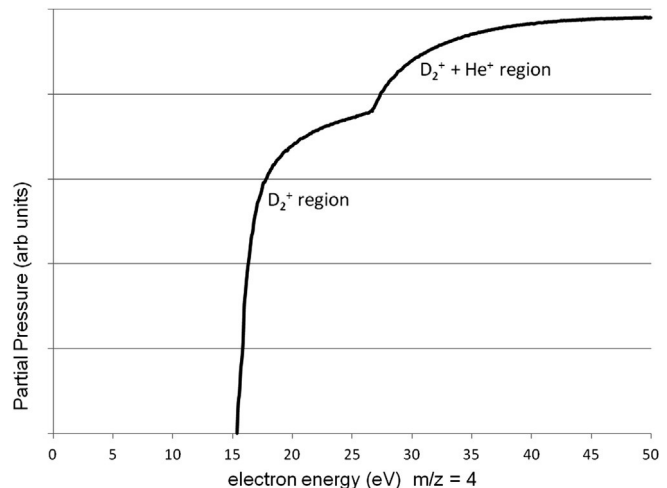


Fig. 4. TIMS spectral separation of 1:1 D_2 : ^4He mixture at $m/z = 4$ when both gases are present simultaneously. Partial pressure (arb units).

$$N_{(D_2+^4He)} = A_i \left\{ \left(\sigma_{(D_2)}^{31\text{ eV}} \right) \cdot \eta_{(D_2)} + \left(\sigma_{(^4He)}^{31\text{ eV}} \right) \cdot \eta_{(^4He)} \right\} \quad (2)$$

In Equations (1) and (2), $\eta_{(D_2)}$ and $\eta_{(^4He)}$ are the real abundance densities of D_2 and ^4He in the sample gas, $N_{(D_2)}$ and $N_{(D_2+^4He)}$ are respectively the (D_2) and $(D_2 \text{ and } ^4He)$ partial pressure signals combined as measured using TIMS. The constant (σ) is the ionisation cross section co-efficient, and A_i is the instrument factor, which is considered equivalent for both equations as it is measured at the same m/z with the same QMS settings simultaneously. Solving Equations (1) and (2) simultaneously, gives

$$\frac{\eta_{(D_2)}}{\eta_{(^4He)}} = \frac{\left(\sigma_{(^4He)}^{31\text{ eV}} \right)}{\frac{N_{(D_2+^4He)}}{N_{(D_2)}} \left(\sigma_{(D_2)}^{19\text{ eV}} \right) - \left(\sigma_{(D_2)}^{31\text{ eV}} \right)} \quad (3)$$

From the TIMS data, $N_{(D_2)}$ is the D_2 partial pressure signal measured at 19 eV and $N_{(D_2+^4He)}$ is the D_2 and ^4He partial pressure signal combined, measured at 31 eV in the TIMS energy spectrum. In this work, the electron energies 19 and 31 eV were chosen for the somewhat arbitrary reason that they provided reasonably approximate equivalent ionisation cross sections (σ) for the two gases (in this case Helium and Deuterium), such that in the TIMS spectra of Fig. 4 this is reflected in the equivalent curve gradients at 19 and 31 eV. In addition to equal ionisation cross sections, the chosen electron energies also have the optimum ion signal transmissions for both gases commensurate with equal ionisation cross sections. A further insight into this analysis and additional data are given elsewhere [8]. The values for the ionisation cross section constant (σ) were obtained from published data [9]. The real abundance densities $\eta_{(D_2)}$ and $\eta_{(^4He)}$ of D_2 and ^4He in the sample gas, hence are obtained. The function derived in Equation (3) is then a somewhat trivial computation for the mass spectrometer system to automatically calculate the concentrations or ratios of He/D_2 gas mixtures in real time. The technique described here is now routinely used at the JET UKAEA laboratory to calculate the ratio of deuterium to helium during Torus plasma operations [8].

The technique of course is not confined only to the aforementioned two gases, and has since been further applied at JET to deconvolute mass peaks at 3 amu using the same methodology. For any conventional type of mass spectrometry this proves challenging due to the small mass separation (0.0058 amu) of the helium 3 isotope (^3He) and any hydrogenated deuterium (HD). However, this is again proved to be a routine measurement using TIMS as shown in Fig. 5, which shows data from the JET Torus following an Ion Cyclotron heating cycle using ^3He as the minority gas as varying amounts of ^3He were injected into the plasma. (Fig. 5 courtesy of JET, UKAEA).

5. QMS TIMS experiments at elevated pressures

So far, we have described how TIMS could be used with advantage to investigate gas mixtures which are otherwise difficult to study using quadrupole mass spectrometers. For the experiments described, the gas pressures used in the ionisation source of the mass spectrometers were typically from XHV/UHV to about 0.0006 Pa. Using a high source pressure QMS system with pulse ion counting detection that may be used at pressures of up to 0.04 Pa, it has become possible to study the physics and chemistry of collision dominated gas reaction kinetics by operating at these much higher pressures. There are a number of advantages in doing so for the analysis of certain gas mixtures (nitrogen–carbon monoxide and helium–deuterium mixtures, for example), and also in studies of neutral species sampled from plasma processing systems.

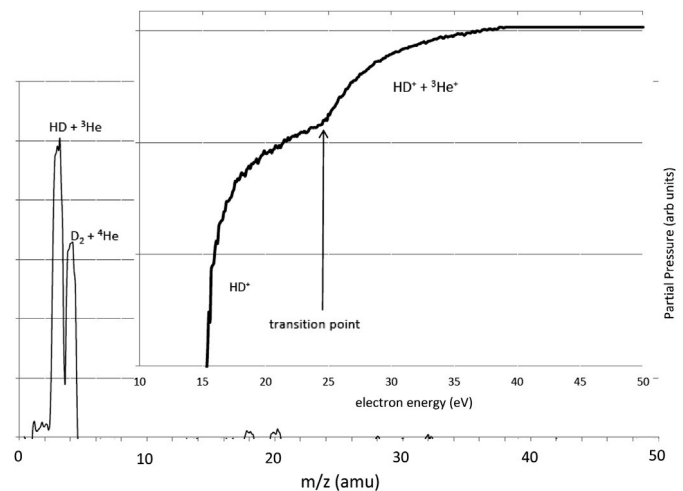


Fig. 5. Conventional mass spectrum obtained at JET showing the convoluted peaks at 3 and 4 amu of HD, D_2 , ^3He and ^4He . The inset figure shows corresponding TIMS separation of HD and ^3He ($\Delta m/z$ 0.0058 amu) at 3 amu. Partial Pressure (arb units). (Courtesy of JET, UKAEA).

For a mixture of nitrogen and carbon monoxide, the mass difference at a nominal m/z value of 28 is small and difficult to separate without significant effort. The possibility of using the TIMS technique has been considered but is difficult to apply since the difference between the threshold ionisation energies for producing N_2^+ from N_2 (15.58 eV) and CO^+ from CO (14.01 eV) [10] is not large and deconvolution of the individual contributions to a given electron energy scan requires care.

Curve A of Fig. 6 shows an energy spectrum at $m/z = 28$ for a mixture containing 1000 ppm of carbon monoxide in nitrogen at a source pressure of 4.10^{-4} Pa. The counts recorded at electron energies below about 14 eV are attributed to the carbon monoxide in the gas sample. When the experiment was repeated, using a different QMS pulse ion counting instrument which had been designed to operate in working pressures of up to 4×10^{-2} Pa, the contribution of the carbon monoxide to the energy spectrum was more clearly seen, as shown in Curve B. It may be concluded from curve B that the energy resolution of the high pressure QMS was sufficient to distinguish between N_2^+ and CO^+ ions when the electron energy was varied between, say, 13 and 17 eV.

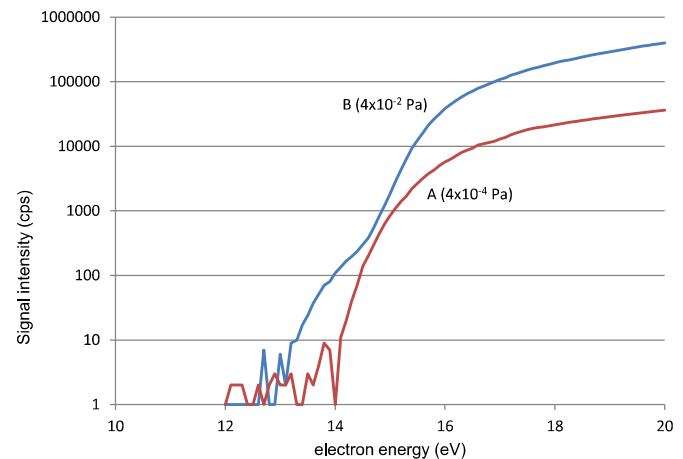


Fig. 6. TIMS spectrum at $m/z = 28$ for a mixture containing 1000 ppm of carbon monoxide in nitrogen at source pressures of 4×10^{-4} and 4×10^{-2} Pa.

Other work by the current authors, not reported here, with the high pressure QMS showed that for the rare gases, and some others such as nitrogen and oxygen, the production of metastable species could be observed. The TIMS mode of operating the mass spectrometer was central for much of this work. Typical measurements for both gas analysis and plasma diagnostics are described below.

6. Gas analysis

For neutral gas analysis the gas samples were admitted directly into the ionisation source of the spectrometer. For pressures up to 5×10^{-4} Pa, electron energy scans for helium were similar to those shown above in Figs. 4 and 5. However, when the source pressure was increased to around 0.01 Pa, TIMS scans for pure helium and pure krypton gave data such as those shown in Fig. 7.

Although not strictly applying TIMS analysis, the form of the spectra shown in the figures of this section are understood with reference to TIMS theory. The onsets of ionisation at 24.5 and 14.0 eV for helium and krypton respectively, are clearly seen, but the curves show additional particle count rates for electron energies below these threshold ionisation values. The recorded signals for electron energies below ionisation threshold are attributed to the formation by electron impact in the ionisation source of metastable helium and krypton, for which the onset electron energies are around 20.0 and 10.0 eV respectively. A proportion of these metastable atoms are not de-excited through collisions with surfaces or in the gas and can travel along the line-of-sight path to the particle detector. The energy resolution of the electron impact source was not capable of resolving the excitation of the 2^1S and 2^3S metastable levels of the helium or of the two krypton metastable levels at 9.9 and 10.6 eV. Fig. 7 also shows that for a helium–deuterium mixture a persistent metastable He^* signal was seen in the TIMS energy spectrum with an onset at around 20 eV, along with the D_2^+ and He^+ thresholds ionisation onsets at around 15 and 24.5 eV respectively.

Similar scans were obtained for neon and xenon gas samples and were again consistent with the known energies of the metastable levels of these species. It should be noted that the metastable atoms generated in the mass spectrometer source are, of course, uncharged and are, therefore, not mass resolved during their passage through the quadrupole section of the mass spectrometer. They are transmitted at all m/z (mass-to-charge) settings of the

spectrometer. This was confirmed by setting values of m/z (e.g. $m/e = 5.5$ and 9.5) which did not correspond to any ion species present in the system. Electron energy scans obtained for these arbitrary values of m/z still exhibited the signals attributable to the metastable species. For example, for a mixture containing a small proportion of krypton in helium the scan at $m/z = 5.5$ showed the krypton metastables for energies between 10 and 20 eV and then, additionally, from 20 eV upwards a contribution from the metastable helium.

It was at first sight surprising that the particle detector recorded the arrival of all these uncharged species, but we have to conclude that the internal energy of the excited atoms was sufficient for their arrival at the entrance surface of the detector to initiate a countable electron pulse. This view is consistent with the fact that when the inert gas samples were replaced by oxygen, no signal attributable to formation in the source of the mass spectrometer of metastable $\text{a}^1\Delta_g$ oxygen was observed, although the lifetime of these particles is comparable with those of the metastable inert species. The oxygen metastable level is, however, only about 1 eV above the ground state and thus its available internal energy is insufficient to generate a countable electron pulse.

7. Plasma analysis

The high pressure QMS was also used to investigate high pressure plasma processes, where a RF plasma was operated in the reactor as shown in Fig. 8. The plasma was operated at 13.5 MHz at power levels of the order of 10 Watts between parallel plate electrodes. The ion and neutral species produced in the plasma and travelling to the grounded electrode were sampled through a small orifice in the latter. Electrodes behind the sampling orifice could be used to control the entry of ions from the plasma into the mass spectrometer. With pressures in the plasma reactor of around 6.5 Pa, the pressure in the source of the mass spectrometer was typically 0.03 Pa.

With a plasma operating in helium, but with the internal ionisation source of the mass spectrometer turned off, and the sampling system set to prevent any positive ions from entering it, the detector recorded the arrival of He^*_{m} produced in the plasma. The metastable signal was proportional to the plasma power and to the gas pressure in the reactor, as shown in Fig. 9. When the helium plasma was replaced by one operating in oxygen, no energetic

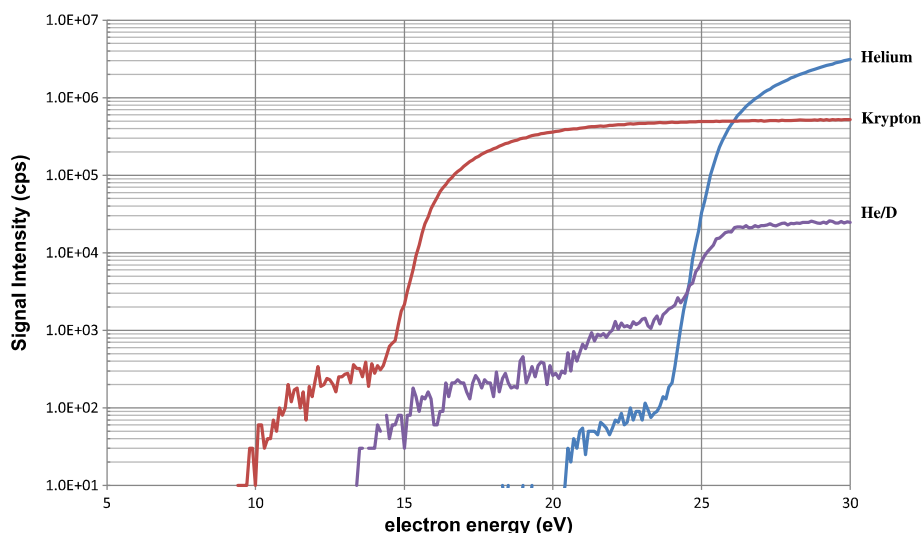


Fig. 7. TIMS response ion counts per second (cps) at high source pressures showing the presence of both metastable neutral atoms and ionisation threshold onsets of Helium and Krypton noble gases.

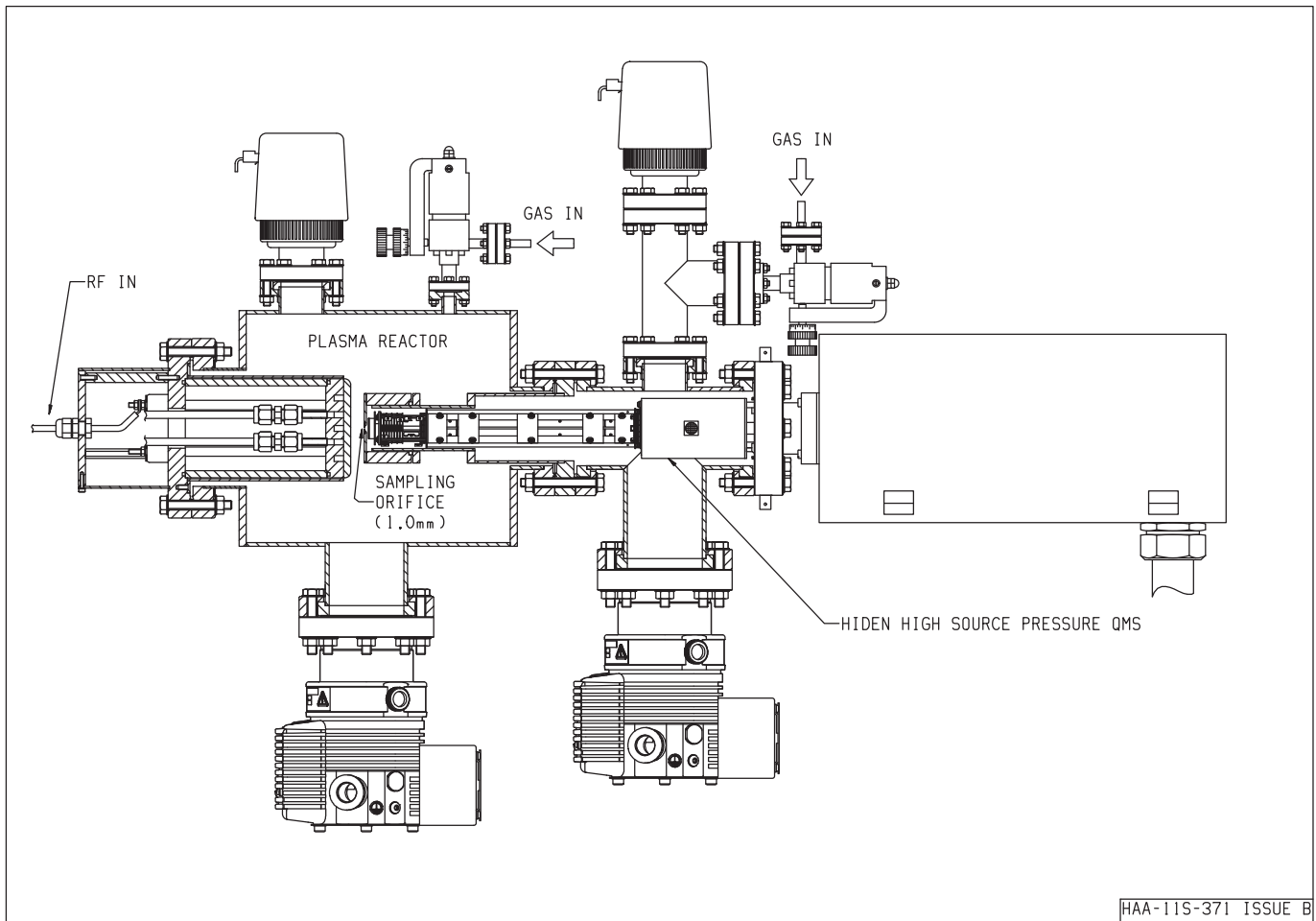


Fig. 8. RF plasma source and high pressure QMS.

particles from the plasma were detected. This result was as anticipated since any metastable $a^1\Delta_g$ oxygen produced in the plasma, although having a long life-time against spontaneous decay, had insufficient internal energy to be recorded on arrival at the detector or was destroyed by collisions during passage through the system.

With the plasma operating in a mixture of helium and oxygen, with all plasma ions rejected as before by the sampling system, but with the internal spectrometer source now turned on, the electron energy scans at $m/z = 4$ for detection of He^+ ions were of the form shown by curve ABC of Fig. 10.

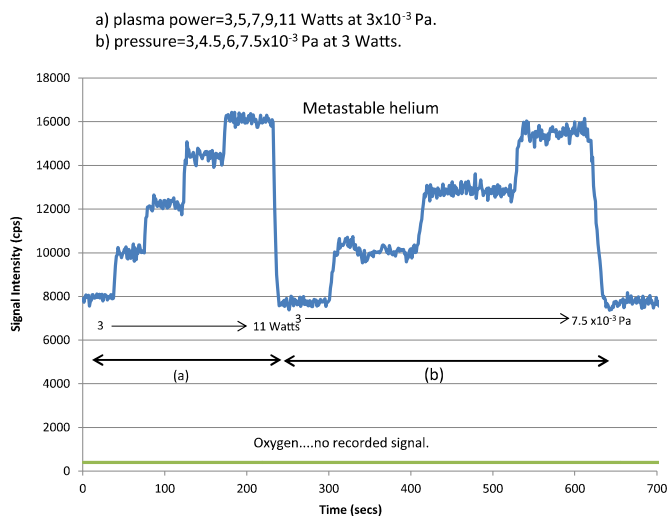


Fig. 9. TIMS detection of metastable helium produced in a 13.56 MHz RF plasma.

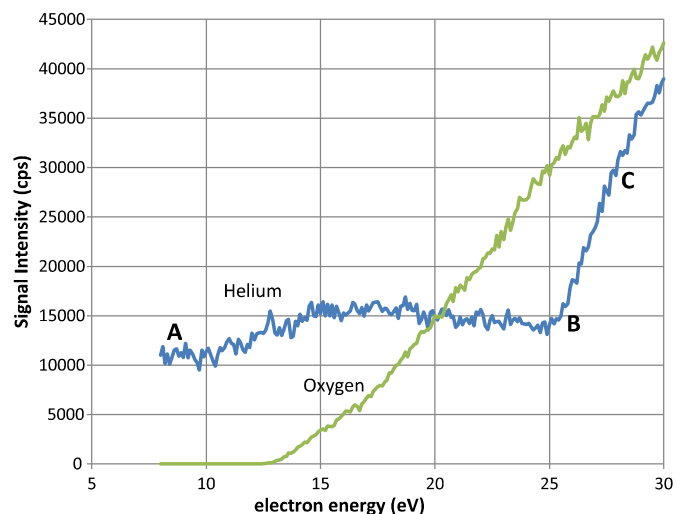


Fig. 10. TIMS detection of metastable $\text{He}^* m$, and He^+ ions with a 13.56 MHz RF Plasma and the high pressure ion source operating.

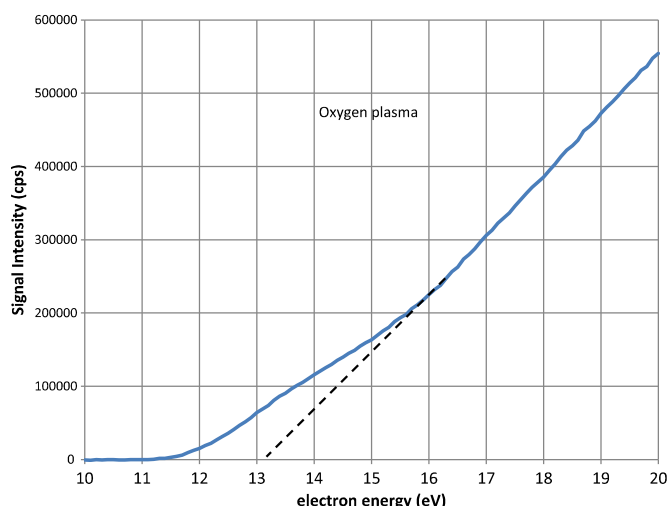


Fig. 11. TIMS from 13.56 MHz RF oxygen plasma.

The section BC of the curve for helium represents ions produced in the source of the mass spectrometer, from ground state helium atoms, by electrons with energies above 24.5 eV. The section AB represents helium ions produced in the source by electron impact on metastable helium atoms produced in the plasma and sampled in the same way as the ground state atoms. The threshold electron energy for this process is expected to be around 5 eV, which was below the minimum electron energy of 8 eV which could be used in the present work. For electron energies above 20 eV there is expected to be a small contribution to the recorded count rates by metastable helium created in the ionisation source, but this small contribution was removed by subtracting from the raw data the counts recorded at $m/z = 9.5$, which, as explained earlier, are a direct measure of this metastable signal. Fig. 10 also includes a curve for $m/z = 32$ (oxygen ions). There is no evidence of ion formation from metastable $a^1\Delta_g$ oxygen at electron energies below the onset energy for ionisation of ground-state oxygen or through Penning ionisation in the source in collisions between metastable helium and neutral oxygen molecules.

When the experiment was repeated with pure oxygen instead of the helium/oxygen mixture, a 15 Watt plasma at a pressure of 4 Pa and a source pressure of 0.03 Pa gave electron energy scans of the form shown in Fig. 11.

The region below 16 eV appears to have two components with onset energies that differ by about 1 eV. This is to be expected if either sufficient metastable oxygen is sampled from the plasma or produced in the source. Subsidiary experiments suggested that for the experimental conditions of Fig. 11 the latter possibility was the more likely. In principle, however, it would clearly be possible to use the TIMS ionisation technique for more intense plasmas to examine the rate of production of metastable oxygen as a function of the plasma conditions.

There have been previous TIMS investigations of nitrogen plasmas in which metastable species have been studied. Matsuda et al. (2004) [11] investigated a 10 mA DC plasma at 400 Pa and compared the TIMS signals obtained for electron energies between 8 and 24 eV at $m/z = 28$ with and without a plasma operating. For electron energies in the range 8–15 eV, the data were interpreted as showing the production of $N_2(A^3\Sigma^+ u)$ nitrogen in the plasma

and were compared with cross-section data reported by Armentrout et al. [12] for ionisation of that excited state. The data of Armentrout et al. were consistent with a threshold energy of 10.1 ± 0.6 eV compared to the theoretical value of 10.47 eV for ionisation of the excited nitrogen to the $A^3\Pi^+ u$ state of N_2^+ .

The ability of the instrument to monitor the production of long-lived excited species in a plasma, provided they have sufficient internal energy, is clearly a potentially useful development in the mass spectrometry of processing plasmas.

8. Conclusions

It may be concluded from the results described here for a number of challenging problems, which are well known in conventional mass spectrometry, that significant advantages are obtained if electron energy spectra for production of particular positive ions are measured in addition to conventional mass spectra obtained at a single, normally high, electron energy (70 eV). Threshold ionisation measurements are particularly instructive and may be used to separate signals from species with essentially identical ion masses if the ionisation potentials of the two or more target species are separated by more than, say, 1 V. The determination of the relative abundances of these gases is, therefore, significantly simplified.

Applications of threshold ionisation mass spectrometry in conjunction with high pressure mass spectrometers fitted with suitable particle detectors have demonstrated the benefits which result from the possibility of reducing the pressure differential between reactors, such as those used for plasma processing of materials, and the mass spectrometer used to examine the neutral and ionised species formed in such plasmas. There are obvious simplifications in the pumping arrangements required for the diagnostic systems. Other, less expected, benefits which result from reactions in the ionisation source of the mass spectrometer have also been observed, and suggest possible novel applications. An important conclusion following from the description of data obtained using plasmas generated in gases such as the inert gases and oxygen is that the production of long-lived metastable species in plasma reactors may be studied as a function of the plasma operating conditions.

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