De-Convolution of Complex Residual Gas Spectra at JET

*T. Coyne[1], S. Davies[2], N. Balshaw[1], A. Miller[1], C. Robertson[2], C. Whitehead[1] and EFDA JET contributors**

[1]EURATOM/UKAEA Fusion Association, Culham Science Centre, Oxon. OX14 3DB. UK
[2]Plasma & Gas Analysis Division, Hiden Analytical Ltd. 420 Europa Boulevard, Warrington. WA5 7UN, UK
*See annex of F Romanelli et al, "Overview of JET Results", (Proc. 22nd IAEA Fusion Energy Conference, Geneva, Switzerland (2008))

INTRODUCTION

At JET, fusion fuel most commonly used in the tokamak is deuterium. Purity of the fuel is vital to ensure the data obtained from plasma pulses is useful, and that pulse recipe repeatability is not compromised.

Our primary goal was to determine the purity of the fuelling gas, deuterium, and confirm that we did not have any contamination from helium (He). Analysis using our quadrupole Residual Gas Analysers (qRGA) in the conventional way was not possible due to the overlapping masses of the two species at 4 atomic mass units (amu).

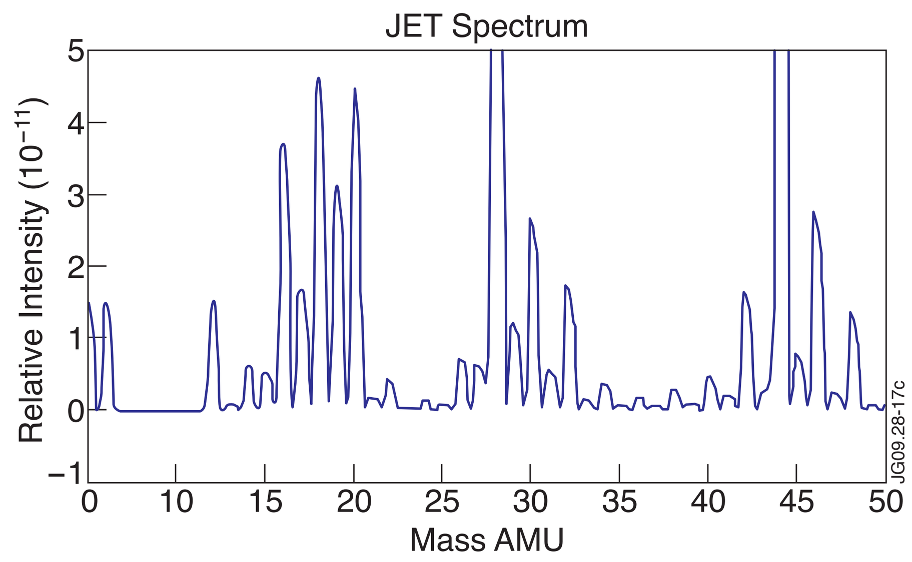
Here, we present and demonstrate the approach we used to solve this problem; a complimentary technique, Threshold Ionization Mass Spectrometry (TIMS), operating the qRGA mass spectrometer in a mode allowing control over the energy of the electrons emitted within the ionization source.

Recognising the potential to identify more complex compounds which have brought uncertainty when attempting to interpret data from the torus primary vacuum vessel we have applied this technique across a broad range of gases that exhibit overlapping masses in the laboratory.

JET is unique due to the many interacting species.

- 3 isotopes of hydrogen isotope: hydrogen, deuterium and tritium.
- 2 isotopes of helium: ^3He, ^4He
- 3 isotopes of water, H_2O/ heavy water, D_2O / super heavy water, T_2O.
- 6 Tonnes of carbon tiles, complex carbon / hydrogen isotope interactions.

Baking the vessel to 320°C further complicates an already difficult task due to dissociation of C_xH_y and C_xD_y species from the vessel wall.



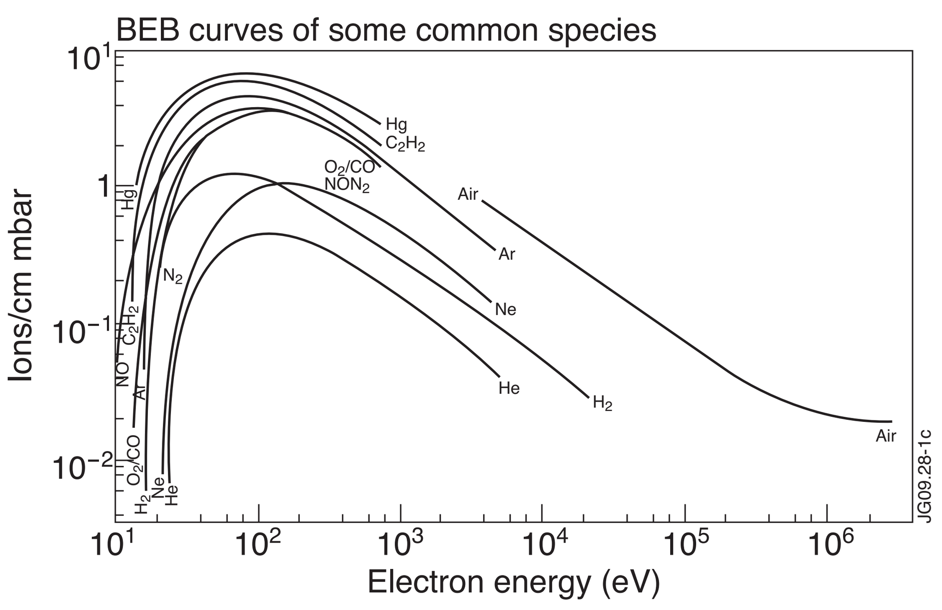
JET spectra at 320°C

Spieces	Major m/z	% Abundance
H_2	2	100
He	4	100
D_2	4	400
CH_4	16	100
H_2O	18	100
D_2O	20	100
CD_4	20	100
Ne	20	100
Air	28	100
CO	28	100
C_2H_6	28	100
C_2D_2	28	100
C_3H_8	28	100
C_2H_4	28	100
N_2	28	100
C_2D_4	32	100
C_2D_6	32	100
O_2	32	100
C_3D_8	34	100
Ar	40	100
C_3H_4	40	100
C_3H_6	42	100
C_4H_{10}	43	100
CO_2	44	100
C_3D_4	44	100
C_3D_6	46	100
C_4D_{10}	50	100

Table of overlapping species

Experimental Details of TIMS at JET

The Hiden Analytical qRGA system at JET is operated in a mode where the energy of the electrons emitted within the ionization source is variable. Different elements have defined ionization energies required to remove an orbiting electron. This energy is dependent on the electron orbital, i.e. outer shell electrons generally have weaker ionization energies due to the greater distance and lower electrostatic forces from the nucleus. This gives rise to the electron impact "threshold ionization energy" curve. The ionization process of neutral particles commences at a minimum (threshold) energy of the impacting electrons. This minimum energy is dependent and unique to any species present in the gas matrix, resulting in a spectral "identifier" or fingerprint for all atomic or molecular species.



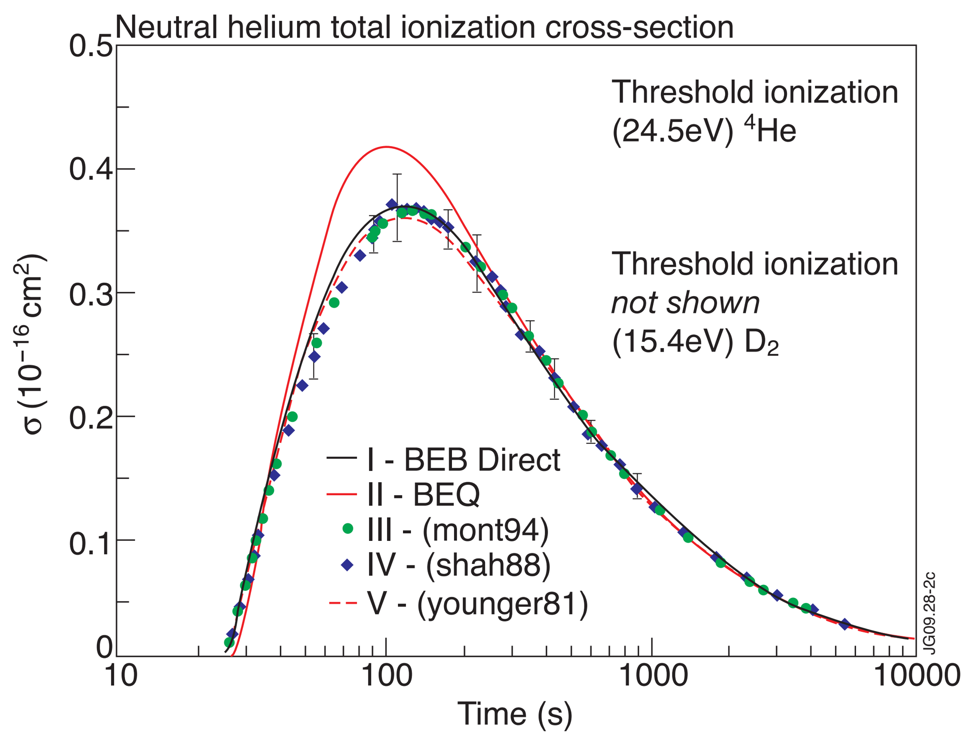
Halzoric and Test chamber

Experimental Method

- Hiden Analytical HAL201 RC qRGA mass spectrometers interfaced to test chamber at JET. Total system pressure held at ~10^{-7} mbar during data collection.
- Gas mixtures introduced through the test chamber with Mass Flow Controllers (MFC) to allow user control of the ratio of individual species within the matrix. (MFC accuracy ± 1%).
- Gas species in the test chamber (mixed using the MFC's); ultra pure (100%) D_2, (100%) ^4He, and small (1%) concentrations of CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10} in (94%) N_2 carrier gas.

Experimental Aims

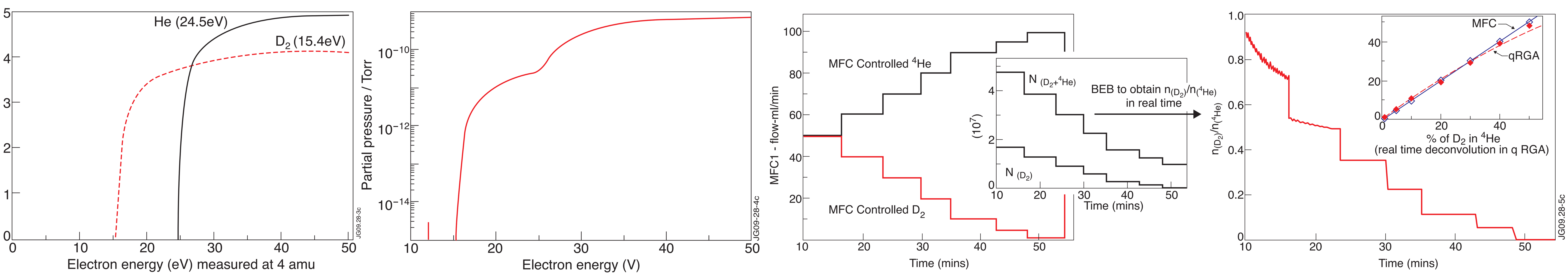
- Mix D_2 and ^4He and control ratio of the mixture with MFC's. Investigate the possibility of de-convolution of D_2 from ^4He at 4amu in the mass spectrum, and real-time quantification analysis techniques using the qRGA TIMS technique, combined with BEB ionization cross section (σ) theory.
- Mix D_2 with the hydro-carbon mixture to investigate the possibility of TIMS de-convolution of complex H_xD_y, C_xH_y, C_xD_y, and preliminary real time qualitative data analysis. Investigate D_2O formation and de-convolution at 20amu



Gas inlet system

Results: TIMS De-convolution of $^4He/D_2$ Gas Mixture at JET

The figure below shows real time mass flow controlled ratio of $^4He/D_2$ gas mixture displayed within qRGA software. The inset on the left shows the corresponding raw qRGA data [at 4amu] taken as a function of time. The two traces represent $N(D_2)$ and $N(D_2 + He)$ at 19eV and 31eV respectively. The real time qRGA data on the right shows the true $^4He/D_2$ abundance ratio $n(D_2)/n(He)$ after applying BEB theory in the qRGA software.



Application of the BEB threshold ionization cross section theory to qRGA data:

From theory, $N_{(D2)}$ is the D_2 partial pressure signal measured at 19eV and $N(D_2 + He)$ is the D_2 and ^4He partial pressure signal combined, measured at 31eV in the qRGA. Now, $\eta_{(D2)}$ and $\eta_{(He)}$ are the real abundance densities of D_2 and ^4He in the sample gas. To obtain the ratio, $n_{(D2)}/n_{(He)}$ from the measured partial pressure signals $N_{(D2)}$ and $N_{(D2 + He)}$, to a first approximation it can be shown;

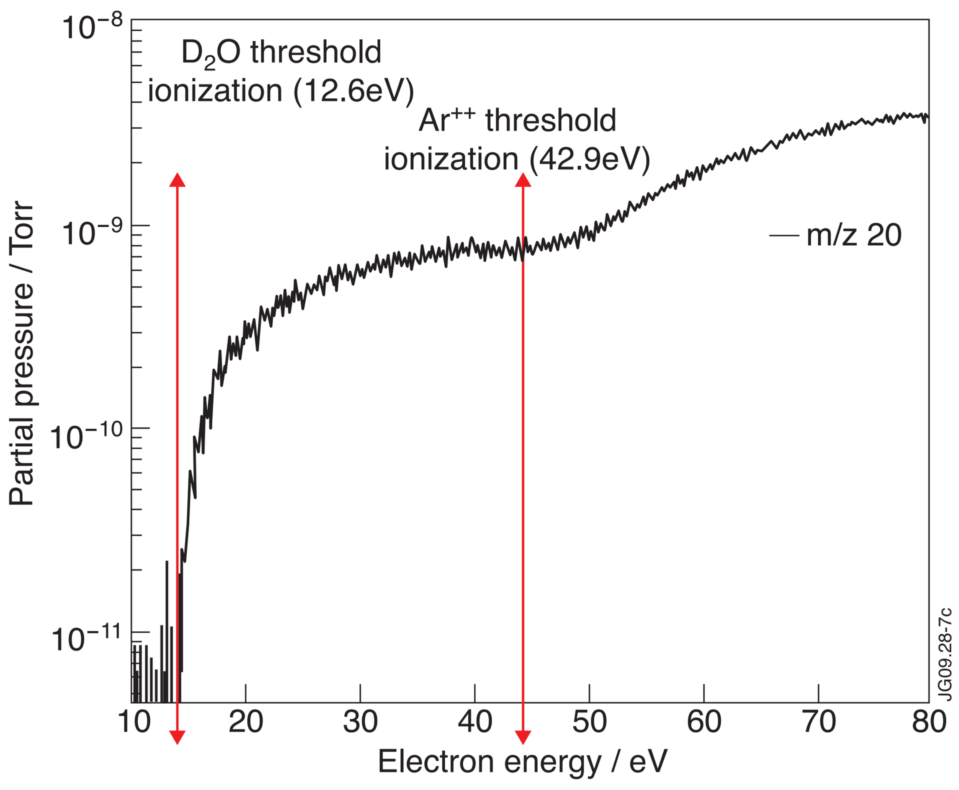
$$N_{(D_2)} = A_i \left(\sigma^{\{19eV\}}_{(D_2)}\right)_0 \cdot \eta_{(D_2)} \quad (1), \qquad \text{and similarly,} \qquad N_{(D_2+{}^4He)} = A_i \left\{ \left(\sigma^{\{31eV\}}_{(D_2)}\right) \cdot \eta_{(D_2)} + \left(\sigma^{\{31eV\}}_{({}^4He)}\right) \cdot \eta_{({}^4He)} \right\} \quad (2)$$

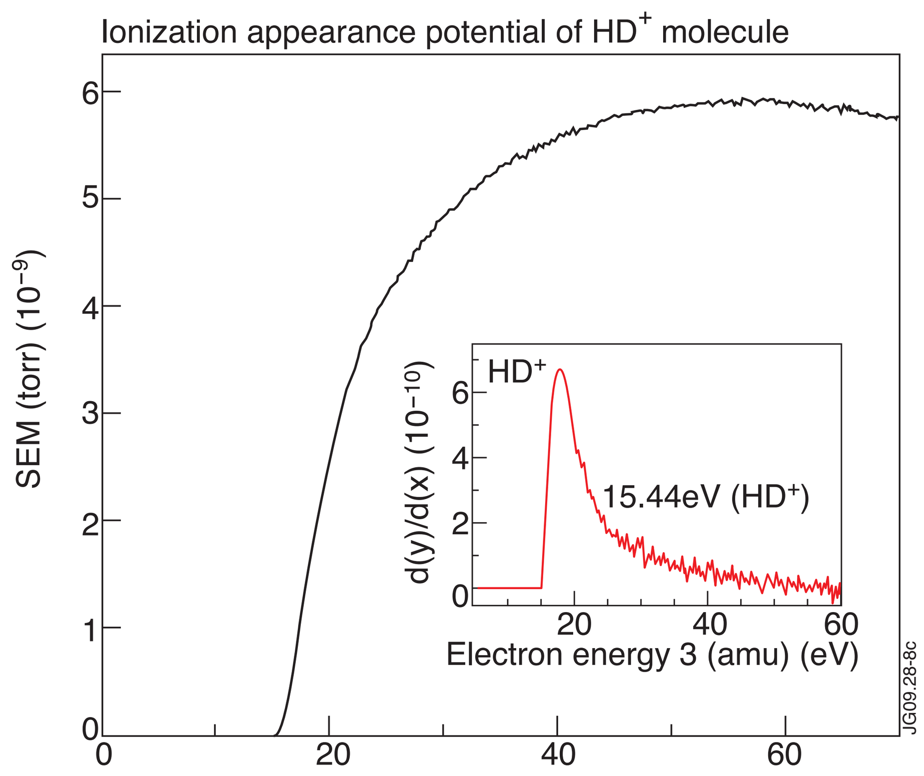
A_i is the instrument (qRGA) factor which is the same for both D_2 and ^4He as the signal is measured at m/z = 4amu. It is also independent of electron ionization energy between energies of 19 and 31eV. Also, we define the ionization cross sectional coefficients for D_2 and He as $\eta_{(D2}$ and $\eta_{(He)}$ respectively: Solving (1) and (2) yields;

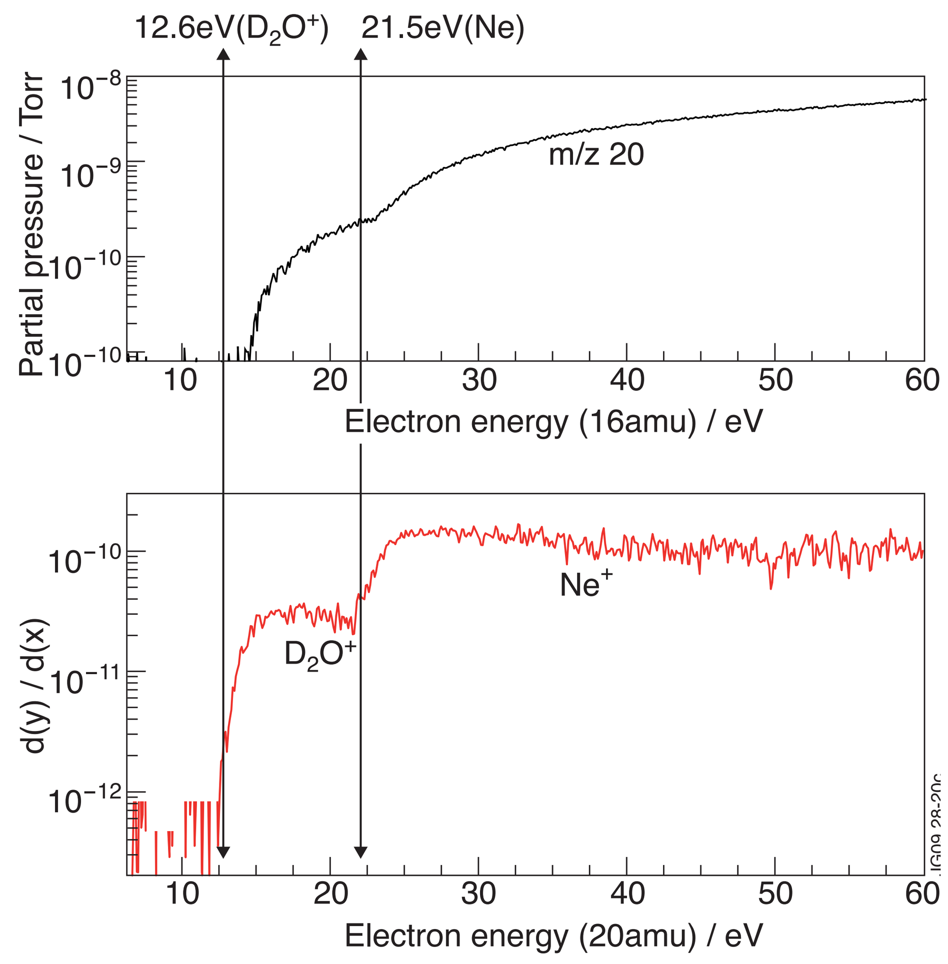
$$\frac{\eta_{(D_2)}}{\eta_{({}^4He)}} = \frac{\left(\sigma^{\{31eV\}}_{({}^4He)}\right)}{\frac{N_{(D_2+{}^4He)}}{N_{(D_2)}}\left(\sigma^{\{19eV\}}_{(D_2)}\right) - \left(\sigma^{\{31eV\}}_{(D_2)}\right)}$$

TIMS de-convolution of ≤1% heavy water (D_2O) from doubly ionized argon (Ar) at 20 amu.

The figure below shows separation of small (<1%) quantities of heavy water from chamber residual Argon.
Neon (Ne) at mass 20 has also been separated in this way which is a useful tool to identify leakages from the JET torus interspaces which are filled with this gas
It can also be seen that TIMS clearly identifies formation of HD+ molecule at 3amu via the onset at 15.5eV.
This will allow confident de-convolution from T^+ (3amu) when Tritium is introduced into the JET fuel mixture.
(note the inset shows the derivative of the TIMS HD^+ curve to qualitatively further enhance species de-convolution in the TIMS spectra)





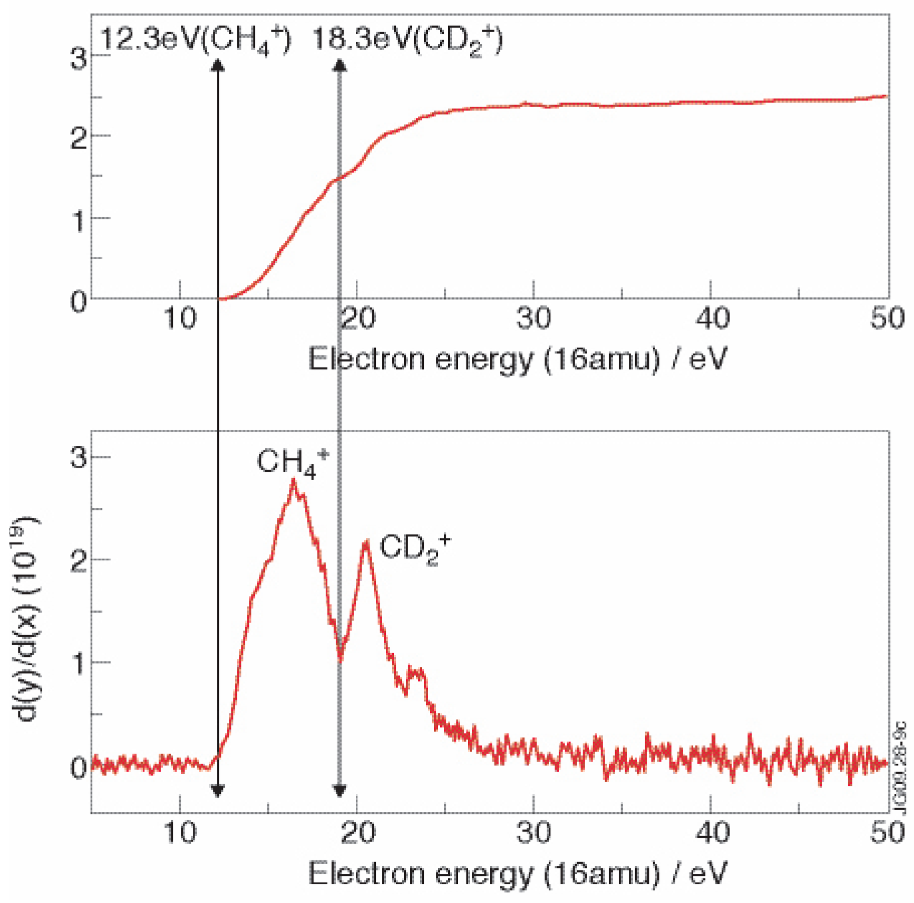


Preliminary results show interaction of Deuterium (D_2) and hydrocarbons resulting in the formation of C_xH_y and C_xD_y molecules. For example at 16amu, overlapping species are CH_4^+ and CD_2^+. TIMS onsets are 12.3eV and 18.24eV respectively. Below species de-convolution is shown with TIMS. The differential;

$$\frac{dy}{dx} = \frac{d(partialpressure)}{d(electronenergy)}$$, (dy/dx) is shown simply to

qualitatively enhance the de-convolution of the transition regions, with the minima in the corresponding to the transition from CH_4^+ + to ($CH_4^+ + CD_2^+$)

In the figure on the right, the hydro-carbons in the 50:50 D_2/(N_2 carrier gas) are present at just a 0.5% fraction of the gas mixture total composition, also demonstrating a use for low level impurity detection.



Neon (Ne) at mass 20 has also been separated in this way. The two spectra above show the raw data curve (top) and the derivative (bottom) clearly demonstrating the separation of the D_2O at 12.6eV and Ne at 21.5eV, both sharing the same mass at 20amu. Separation of these masses will prove a useful tool at JET as the vessel interspaces are filled with neon so detection of a leak from one of these into the torus can be identified easily.

Whilst here we have demonstrated findings from some of our first laboratory experiments our success has identified characteristics of many of the species in this table. Occasionally overlapping species may have first ionization energies too close to each other to distinguish with our equipment. These cases are easily overcome but utilising the 2nd or 3rd ionisation energies by increasing the energy of the electrons emitted within the qRGA source to eject orbiting electrons from more tightly bound shells.

This table lists many species showing information of the respective masses that go to form the individual "cracking patterns". Many of the hydrogen and deuterium carbon species have several minor masses due to fragmentation of the molecules within the instrumentation electron bombardment source. As in this case cracking patterns are shown from instrumentation operating with a fixed electron energy of 70eV. The column on the right of the table indicated the 1st ionization potential for each respective species.

CH_4^+/CO_2^+ Tims spectra

Species	Major m/z	%	Major1 m/z	%	Major2 m/z	%	Major3 m/z	%	Major4 m/z	%	Major5 m/z	%	Major6 m/z	%	Rel Sens	1st IE (eV)
H2	2	100														15.42
He	4	100													0.14	24.58
D2	4	400														15.46
CH4	16	100	15	85	14	16	13	5	12	2	17	1			1.6	12.61
H2O	18	100	17	21	16	2									0.9	12.61
D2O	20	100	18	21	16	2									0.9	
CD4	20	100	18	85	16	16	15	5	14	2					1.6	12.65
Ne	20	100	22	10												21.56
Air	28	100	32	27	14	6	40	1							1	
CO	28	100	12	5	16	2									1.05	14.01
C2H6	28	100	27	33	39	26	26	23	29	21	15	5			2.6	11.57
C2D2	28	100	26	17	14	5	24	4	12	1						11.2
C3H8	28	100	26	59	27	41	44	28	43	23	39	19	41	13		10.94
C2H4	28	100	27	64	26	53	25	8	14	2						10.51
N2	28	100	14	15												15.58
C2D4	32	100	28	64	30	62	16	11	26	10	14	6	12	4		10.54
C2D6	32	100	30	24	36	20	28	18	34	16	18	4	16	4		11.73
O2	32	100	16	22												12.06
C3D8	34	100	32	60	30	30	50	22	42	16	46	12	28	7		11.4
Ar	40	100	20	16											1.2	15.75
C3H4	40	100	39	80	38	30	37	20	36	5	41	4				10.36
C3H6	42	100	39	73	44	70	27	39	40	29	38	20	37	13		9.73
C4H10	43	100	29	44	27	40	28	32	41	40	39	14	58	13		10.53
CO2	44	100	16	9	28	8	14	8	22	3					1.4	13.79
C3D4	44	100	16	89	40	35	38	27	36	8	26	4				10.37
C3D6	46	100	42	74	48	70	30	39	44	30	40	20	38	13		9.76
C4D10	50	100	34	44	30	37	32	37	46	28	42	13	48	12		10.5

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Conclusions and Future Work

Using the qRGA TIMS technique, de-convolution of the mass spectra obtained at JET could lead the way to providing a better understanding of the chemistry within the vacuum vessel, as well as providing invaluable diagnostic information during vessel conditioning.

Initial TIMS has proved encouraging, demonstrating discrimination of $D_2/^4He$ (4amu) and D_2O/Ar^{++} (20amu). De-convolution of C_xH_y and C_xD_y molecules in the mass spectrum is ongoing, with initial results de-convoluting CH_4^+ and CD_2^+ (16amu). With application of BEB to TIMS, we have demonstrated the generation of algorithms within the qRGA software to automatically discriminate different species quantitatively with overlapping peaks in the mass spectra.

Further experimental work will continue using our dedicated gas inlet with the addition of a carbon reaction cell to study the dissociation of species with temperature as well as generate C_xH_y and C_xD_y species to obtain further TIMS data for the purpose of improving the technique.

In addition to this the installation of the Hiden HAL201 RC qRGA is taking place on the JET Gas Introduction System Matrix and on the JET torus. From these instruments we hope to prove our de-convolution algorithms to give an accurate breakdown of the composition of the complex residual gas spectea at JET.

2010 brings the installation of the beryllium plasma facing wall at JET and an opportunity to accurately determine the vessel chemistry during commissioning. The results from this phase of JET operations and further applications of the technique including leak detection and cryogenic pump regeneration inventory determination could prove valuable for ITER commissioning and operations.

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