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Detection of ammonia by residual gas analysis in AUG and JET

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***See the Appendix of F. Romanelli et al., Proceedings of the 25th IAEA Fusion Energy Conference 2014, Saint Petersburg, Russia*

Nitrogen seeding, necessary for divertor heat-load mitigation in ITER, has been shown to lead to ammonia formation which would be a severe operational and safety issue in ITER. Predictions of ammonia production in ITER are based on data from present day fusion devices. Ammonia is mainly detected by residual gas analysis (RGA). Detection of ammonia is impeded by the presence of water and methane which, in a mixed H-D system, leave signatures in the same range of the mass spectra. A statistical model is used to ascribe an average isotope ratio to each gaseous species. The model is tested with simulated RGA recordings with varying concentration of ammonia to evaluate the sensitivity to fitting parameter boundaries, noise in the recordings and mis-matching cracking patterns. The analysis shows that the fitting procedure may in some occasions substitute species among each other, resulting in faulty concentrations. Nevertheless, the right choice of parameter boundaries ensures correct fitting results. Finally, the fitting procedure is applied to experimental data from nitrogen-seeded discharges at AUG and JET.

Keywords: ammonia formation, nitrogen seeding, residual gas analysis.

1. Introduction

In tokamaks with full metal first wall, impurity seeding is required to maintain a high level of plasma confinement and control the divertor power load[1, 2]. For ITER, nitrogen is considered as most suitable seeding species to replace the intrinsic carbon radiation of previous carbon based tokamak configurations[3]. However, nitrogen seeding has been proven to lead to ammonia formation[4, 5]. This is a potentially severe issue for the operation of ITER in the active phase as suitable procedures will have to be developed to release the tritium stored in the ammonia molecules both from the in-vessel surfaces and cryo panels, as well as in the tritium processing plant. The mechanisms of ammonia formation in the complex environment of a fusion device are still fairly unknown and currently, the main data for predictions of ammonia formation in ITER is expected from experiments in present-day fusion devices with full-metal plasma facing surfaces.

In the research results reported so far, the prime diagnostic of in-vessel produced ammonia was residual gas analysis of the exhaust gases. Although the fusion devices operated predominantly with deuterium, the

detected ammonia showed a considerable amount of hydrogen, indicating isotope exchange on the path from the area of formation to the location of the mass spectrometers. Also present were methane and water, each with its own, sometimes varying, isotope configuration. In general, each species could appear as any of its isotopologues, increasing the number of different molecules to 12, while the RGA data provides only 6 independent signals as the relevant intensities are found in the 15 – 20 AMU range. In order to reduce the number of fitting parameters, a statistical model which assumes an average isotope ratio in each species, was developed. Each species is described with only two parameters: the partial pressure and the H/(H+D) ratio (average number of H atoms in a molecule, divided by the total number of H and D atoms). The number of fitting parameters is then reduced to 6, which, in theory, makes it possible to resolve each molecule from the RGA recording. In this contribution, we present an analysis of this analytical tool and the thusly identified limitations and capabilities.

2. Analysis of RGA recordings

2.1 Statistical model

As a molecule enters the stream of energetic electrons in the ionization chamber of the mass spectrometer, it is ionized and often partly dissociated. Thus, the mass spectrometer detects not only the main molecular ion but also ions of molecular fragments. In the case of ammonia, water and methane alike, the fragments are formed by stripping of one or more hydrogen (or deuterium) atoms from the molecule. The relative intensities of the resulting peaks in the recorded mass spectra, related to the probability for dissociation of the molecule, are known as the cracking patterns.

The presence of both hydrogen in the molecule is reflected in the cracking patterns: the peaks shift to appropriate masses, and additional peaks appear as stripping of one (or more) atom from the molecule can result in different numbers of D and H atoms in the remaining molecular fragment (depending on whether a D or H atoms has been stripped). However, the probability for dissociation is not crucially affected by the isotope configuration, as has been experimentally confirmed for ammonia and water[6-8]. It should be noted that the model used in these analysis takes into account only the removal of the first two hydrogen/deuterium atoms from the molecule.

The probability that a molecule appears in the isotope configuration with n H atoms is expressed by the binomial probability distribution:

$$P(p, n, k) = \binom{n}{k} p^k (1-p)^{n-k}$$

where p is the H/(H+D) ratio and k is the number of all H or D atoms in the molecule. Thus the isotope configuration of the molecule, $M(p)$, is expressed as:

$$M(p) = \sum_{n=0}^k P(p, n, k) M_n$$

where M_n is the cracking pattern of the isotope configuration with a number k of H atoms from a total of n of all H or D atoms in the molecule. Using the model, a set of equations is constructed:

$$S = \sum_{m=15}^{21} (\text{model}@m - \text{recording}@m)^2$$

Where $\text{model}@m$ is the modeled intensity at each mass, expressed as a function of partial pressures and isotope ratios of the considered molecules, and $\text{recording}@m$ is the measured intensity at each mass. The least squares fit is carried out with the minimize function of the scipy.optimize python library, using the L-BFGS-B method.

2.2 Model RGA recordings

To verify the operation of the fitting procedure, a RGA recording is synthesized, similar to the recordings which are obtained in during plasma discharges. Rather than mimicking exact evolutions of the signals however, these timetraces are based on constant pressures of methane and water, and a linearly increasing partial pressure of ammonia. Such behavior allows for a more systematic observation of the efficiency of the fitting procedure.

The values of the set partial pressures are based on typical values found in JET discharges, and are normalized to the pressure of methane, which was found to be the most prominent impurity in non-seeded discharges[4]. The partial pressures of methane and water are thus 1.0 and 0.375 respectively, with the partial pressure of ammonia rising from 0 to 2 over the course of 10 seconds. The H/(H+D) ratios are set at 0.05 for methane, 0.2 for water and 0.5 for ammonia. Similar impurity content, and a high H/(H+D) ratio in ammonia have also been observed at AUG[5]. The intensities are calculated using cracking patterns provided by Hidden Analytical[9].

2.3 Fitting in ideal conditions

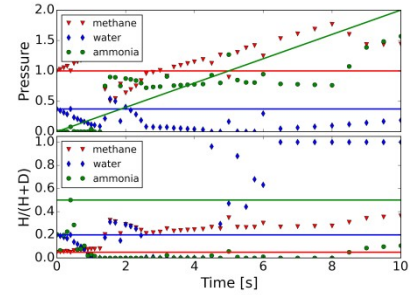


Fig. 1. Results of fitting a noiseless signal, using exact cracking patterns, with free H/(H+D) ratios

The ideal conditions for the fitting are defined as the complete absence of noise in the RGA recordings, and a perfect match of the cracking patterns used in the analysis to those used to synthesize the recordings. The latter, in analyzing experimental data, translates to using perfectly calibrated devices.

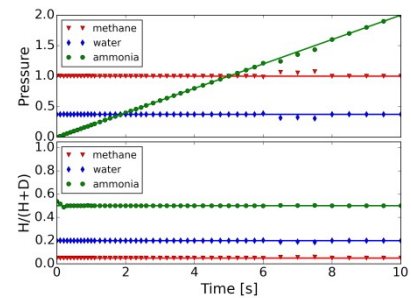


Fig. 2. Results of fitting a noiseless signal, using exact cracking patterns, with the methane H/(H+D) limited.

Even in these ideal conditions, the fitting procedure shows its limitations when a fit is attempted without any restrictions to the isotope ratios. Then, the molecules are substituted among each other which results in incorrect evaluations of the partial pressures, as seen in Fig. 1. In

the first data point, with no ammonia in the gas mix the fit returns correct values. However, as the pressure of ammonia rises, the evaluated pressures of methane and water steadily deviate from the actual values, while the evaluated pressure of ammonia remains 0. The first non-zero evaluation of the ammonia partial pressure occurs when the actual partial pressure of ammonia is around 0.3, however even past that point the trends of the evaluated pressures do not follow the actual pressures. The evaluated partial pressure of ammonia roughly stays constant while the evaluated partial pressure of methane increases to accommodate for the increasing partial pressure of ammonia. Mismatching H/(H+D) ratios are another indication of the substitution of molecules in the fit.

The substitution of molecules in the fit could be prevented by limiting the H/(H+D) ratios of the candidate molecules. The H/(H+D) ratios are in general a quantity that is being investigated by the fitting procedure and restricting their values runs the risk of guessing the values incorrectly. Methane, however, has been shown to exhibit very low H/(H+D) values in D₂ plasmas (ref: Drenik JNM), so limiting its H/(H+D) value in the fit should not lead to erroneous fits.

As shown in Fig. 2, by restricting the H/(H+D) ratio of methane to values between 0 and 0.1, the fitting procedure provides correct results. Some fluctuations persist, however those are limited to a 10 % error margin.

2.4 Impact of noise

To evaluate the impact of noise, random values are superimposed over the synthesized timetraces. The amplitude of this randomization (0.02, normalized to methane) is chosen to match the noise levels identified in RGA recordings at JET (Drenik JNM).

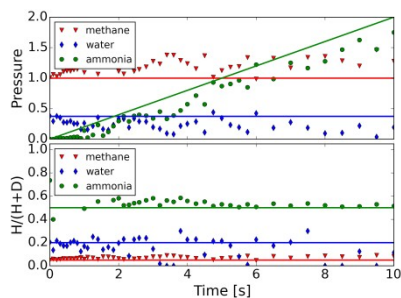


Fig. 3. Results of fitting a noisy signal

Using the H/(H+D) ratio boundaries set in the previous section, the fitting procedure returns somewhat noisy results. The partial pressures still follow the correct trends, however there is a considerable scatter for all three molecules, as seen in Fig. 3. As a consequence of partial substitution between the molecules, the partial pressure of methane is over-estimated by 0.2, which is made up by a reduction of the water and ammonia partial pressure.

The scatter and mis-estimation of the partial pressures virtually vanishes when the H/(H+D) ratio of methane is

further reduced and set as a fixed value to 0.05, as shown in Fig 4a. However, by setting it to a slightly wrong value, (0.0), the methane again substitutes ammonia and water in the fit, resulting in an underestimation of methane and overestimation of ammonia and water, as shown in Fig 4b.

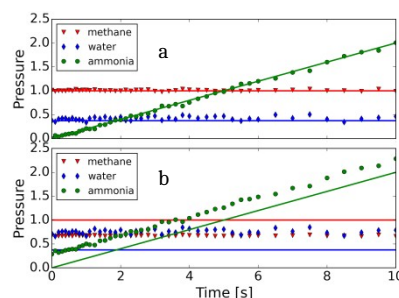


Fig. 4. Results of fitting a noisy signal, with the correct (a) and mis-matched (b) methane isotope ratio.

2.5 Impact of mis-matching cracking patterns

Another uncertainty which affects the analysis of the RGA recording is the mismatch of cracking patterns used in the model. A recent calibration of RGAs at AUG showed that the cracking patterns varied considerably in all of the calibrated devices, and from the values specified by the manufacturers. Thus, it is reasonable to expect that the cracking patterns used in the model will differ to a certain degree from the actual cracking patterns of the measuring device.

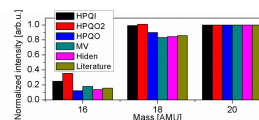


Fig. 5. Cracking patterns of CD₄, recorded with various devices at AUG. “Literature” refers to [9]

To evaluate the impact of these deviations, the model was provided with perturbed cracking patterns: the relative intensity of the 2nd and 3rd peak for each molecule were modified as:

$$I = I_0 P_A R$$

where I is the modified intensity, I_0 is the intensity of the peak in the cracking patterns used to simulate the RGA recordings, P_A is the amplitude of perturbation and R is a random number between -1 and 1 . For each amplitude of perturbation, the procedure is repeated a total of 100 times with a randomized cracking patterns, and a new noisy RGA timetrace is synthesized every 10 times.

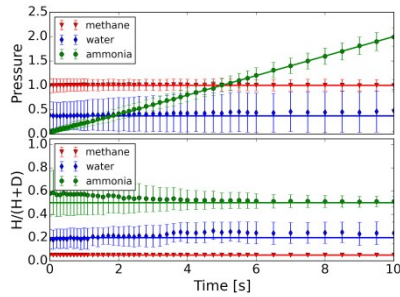


Fig. 6. Average results of fitting with mismatching cracking patterns.

As shown in Fig. 6, even with the highest degree of perturbation, the average fitting results are very close to the actual values, however the error bars increase considerably. The size of the error bars could be considered as a criterion for the threshold of ammonia detection: the reported value of ammonia becomes reliable only when it is so large that it cannot be produced through substitution of other molecules, i.e. the partial pressure of ammonia has to be greater than the sum of the error bars of water and methane. Thus we obtain the evolution of the threshold for ammonia detection versus the magnitude of the perturbation, as shown in Fig 7.

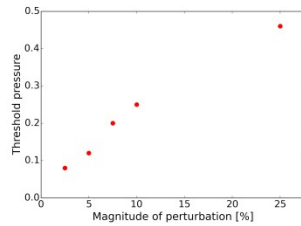


Fig. 7. Threshold of ammonia detection as a function of magnitude of the mismatch of cracking patterns.

2.6 Analysis of experimental RGA data at AUG and JET

The studied fitting procedure is finally used to analyze RGA data from nitrogen-seeded discharges at AUG and JET. Figs 8a and b show plots of RGA data from heavily seeded discharges at AUG and JET respectively. The analysis is based on timetraces from currently uncalibrated devices, which means that it is not possible to reliably assess the absolute pressures, and that there is a likely mismatch in the cracking patterns. The fitting results were obtained by averaging over 100 individual fits with perturbed cracking patterns, with the perturbation amplitude of 10 %. In both cases, the discharge starts with a short non-seeded phase (1 or 2 datapoints) during which the methane and water content can be evaluated. With the onset of nitrogen seeding the partial pressure of ammonia rises above zero or near-zero values. Shortly thereafter, the evaluated partial pressure of water drops considerably, which is an indication that water is substituted for ammonia in the fitting procedure, and that a part of the

evaluated partial pressure of ammonia is in fact due to the water content.

In the fitting results of AUG data, the uncertainty of the fit due to cracking pattern perturbation is fairly small, while in the case of JET data, it reaches up to 20 % for ammonia. This indicates that at lower concentrations of ammonia, the fitting procedure becomes less robust against the mis-matching cracking patterns. Regardless, the evaluated partial pressure of ammonia is above the threshold of reliable detection in each case.

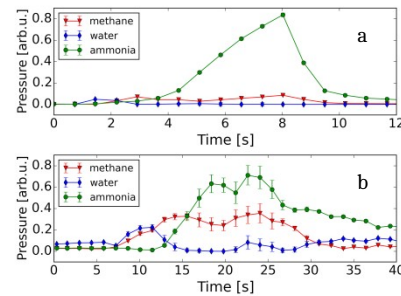


Fig. 8. Fitting results of RGA data in a strongly nitrogen seeded discharge at AUG (a) and JET (b)

3. Conclusions

Assuming an average H/D isotope ratio in methane, water and ammonia allows for the detection of each of the three molecules in RGA recordings made during plasma discharges in fusion devices. However, certain limitations apply to this method of analysis. Even in the ideal condition of a noiseless recording and the use of perfectly determined cracking patterns, the fitting results are strongly influenced by the setting of the boundaries for the isotope ratios (as fitting parameters). Limiting the freedom of these fitting parameters, ammonia can be reliably detected even in adverse conditions (noisy signal, mismatching cracking patterns used in the model). These conditions introduce a threshold value for ammonia below which it cannot be detected reliably. However, in heavily nitrogen-seeded discharges both at JET as well as AUG, the amount of ammonia is above this threshold.

Therefore, the method is of value to study the relative trends in ammonia production, although the absolute values are doubtlessly affected by the uncertainty brought by the noise and mismatching cracking patterns. As the devices which provided the data have not been calibrated yet, it is anyhow impossible to assess the absolute values. In the calibration procedures aimed at determining the sensitivity of the instruments, the cracking patterns should also be measured to reduce this uncertainty.

Acknowledgements

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