

On-line tritiated water detection by in situ ATR-FTIR – Project Summary Report

Project Goals

The presence of tritium in water is challenging to detect given the chemical similarity to hydrogen within the water molecule. Current best practice for detection uses off-line mass spectrometry methods using pre-processing such as flowing afterglow mass spectrometry. This problem has tremendous importance as tritium is one of the top four unabated radioactive emissions from civil nuclear power stations, is a challenge for future fusion reactors and also for waste clean-up, notably at Fukushima where tritium may have to be released to the ocean in the coming years.

We posited that the presence of tritium could be detected due to changes in bond vibrational energies within the water molecule. ATR FTIR is an infra-red spectroscopy technique that can easily be adapted for on-line applications and it promises the possibility of real-time measurement of tritium.

Summary of Results and Findings

We have developed a method utilising an off-the-shelf attenuated total reflectance 'ReactIR' instrument to reliably quantify the isotopic composition of hydrogen within liquid water using deuterium as an analogue to tritium.

The method requires only that the probe is immersed in the liquid sample and we demonstrated fast response within seconds to changes within the deuterium concentration, this is analogous to an in-flow scenario when concentration would change rapidly.

For direct measurement of water, improvements in sensitivity were obtained showing a standard deviation of 47 ppm D. We then achieved a significant breakthrough in discovering that ethanol can act as a chemical signal amplification technique that boosts sensitivity by over two orders of magnitude over the water based technique with standard deviation of the measurement as low as 247 ppb. This improved sensitivity arises from the greater intensity of vibrational absorptions in a deuterated ethanol molecule over a deuterated water molecule. This compares favourably with other more costly and time consuming techniques and is over 20 times more sensitive than any previously published FTIR study.

The experimental data was supported by DFT models. These models produced an excellent fit with the vibrational wavenumbers observed in experiment. With this confidence, the models were used shed light on the vibrational modes present within the chemical signal amplification method and suggested that the improvement in sensitivity arose from a vibrational mode along the carbon spine.

The above results were submitted to the academic journal Nature Scientific Reports in a manuscript titled "Highly Sensitive Real-Time Isotopic Quantification of Water by ATR-FTIR" and we are awaiting the decision following the peer review process.

Our objectives for phase 2 were to assess the translation of the technique to tritium using the modelling approach already developed and to also see whether further improvements in sensitivity were possible. A number of likely signal amplification molecules were screened using the DFT modelling approach considering both the deuterated and tritiated forms focusing on labile protons. Longer chain alcohols gave weaker intensity peak amplitudes and greater noise due to a greater number of vibrational modes present making them poor candidates. Diols such as ethandiol also gave also gave too much overlap between peaks and consequent poor resolution. These findings suggested that we must identify a molecule that would give a smaller number of vibrational modes at high intensity. A molecule termed T-butanol ($(\text{CH}_3)_3\text{COH}$) was identified exhibited perfect

conformational symmetry and would give three detectable peaks distinct for both tritium and deuterium. While promising, there are some challenges to overcome here as the initial experimental results did not match the wave numbers given.

Our second main objective was to develop the model to give quantified outputs for peak intensity that would correlate to concentration of deuterium or tritium in water. Despite much effort we concluded that it was not possible to achieve this using the DFT approach alone and we think that a future technique may be possible by combining together DFT and molecular dynamic simulation which is an ab-initio method which is used to predict bulk physical properties of chemical species. While some initial discussions and meetings were held on this subject, it was not possible to explore this avenue within the scope of the project.

Conclusions

A highly sensitive on-line measurement technique giving a response time in seconds has been developed. Using ethanol as a chemical signal amplification molecule the sensitivity was improved to give a standard deviation of 247 ppb. Modelling by DFT showed excellent agreement with wavenumbers and gave insight into the molecular vibrational modes present. Finally the modelling approach was used to screen many more molecules for effectiveness as a chemical signal amplification agent and to study the effectiveness for use with tritium.

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