The ANSTO ECR Ion Source and its application to mass spectrometry

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Abstract

At ANSTO we have built an Electron Cyclotron Resonance (ECR) ion source to investigate new concepts for mass spectrometers [1,2] designed to measure isotopic ratios in small samples.

ECR ion sources are capable of producing beams of multiply-charged atomic ions with high efficiency and are widely used as heavy ion injectors for accelerators. To meet the requirements of mass spectrometry, we have needed to adapt ECR ion source techniques to our purpose. In this presentation, these and other recent developments of our ECR ion source will be discussed.

Introduction

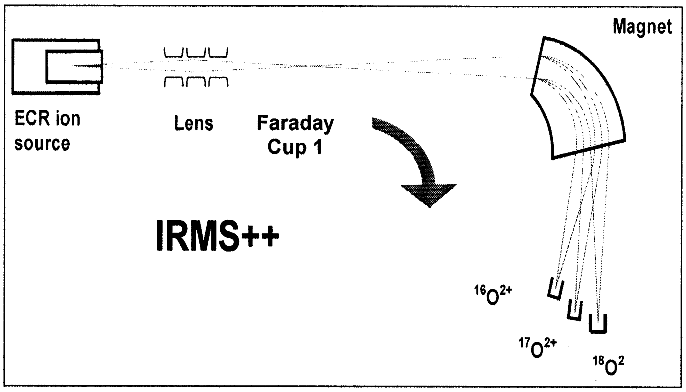

Figure 1: General layout of the IRMS instrument.

Isotopic Ratio Mass Spectrometry (IRMS) techniques are applied to a range of elements to investigate naturally-occurring isotopic ratio variations. Current IRMS systems utilise ionization methods such as Electron Impact to generate ion beams for analysis by a mass spectrometer. This ionization method typically achieves 0.1% ionisation efficiency, dominantly of a 1+ charge state and with little break up of molecules.

Elements for investigation in an IRMS instrument may naturally exist in an atomic state such as noble gases like Argon and Neon, but more commonly as a constituent of a molecule such as oxygen in water. Oxygen isotopes in water cannot be analysed directly due to interferences at the mass values of the rare isotopes ^{17}O and ^{18}O. Interferences are generated by 1+ ions of H_2O and OH, which cannot easily be separated from the rare isotopes. The problem is overcome, in part, by processing of water samples to convert the oxygen component into carbon dioxide gas (CO_2). The ^{18}O/^{16}O ratio can be derived from the ratios of molecular ions at measured at masses 46 and 44. However, ^{17}O cannot be determined in this way, due to the higher abundance of ^{13}C which means that the mass 45 ions are dominated by $^{13}CO_2^+$ ions.

We are using an ECR ion source as an alternative to electron impact ionisation for mass spectrometry. Figure 1 shows the conceptual layout of the ECR based IRMS instrument. Our ECR ion source has been proven to be effective at generating ion beams of multiple-charge state from a range of sample types. This has two major benefits on the IRMS sample process.

First, the process of ionising a molecule to a charge state grater than 1 will lead to most molecules breaking apart, with only very few molecules able to maintain a 2+ charge state. The implication of the molecular break up means that molecules cannot be ionised to high charge states whereas atoms can. Secondly, producing atoms of charge states greater than 1 changes their m/q value. This means that the mass spectrometer is able to effectively separate the multiple charge state atoms free of the parent molecule which can only maintain a single charge state.

In our investigation oxygen, nitrogen, carbon, and argon have been tested in our ECR ion source which has been coupled with an analysing magnet and Faraday cup system to measure mass to charge ratios (m/q) of beams in the range 0 – 120 at a beam extraction energy of 15kV. The efficiency of our enclosed ECR ion source achieves greater than 10%, giving two orders of magnitude improvement on Electron Impact techniques. The removal of sample pre-processing also cuts down of the original sample size required, adding to the overall efficiency of the system.

This investigation of the sample gases has yielded promising results, but has also exposed an issue of sample retention within the ion source as a problem requiring further investigation to reduce the impact of possible memory effects.

ANSTO is working towards constructing a viable IRMS++ instrument for isotopic ratio measurements [2], and further developing a variation on the instrument to allow the measurement of $^{14}C/^{12}C$ ratios free from ^{14}N, $^{12}CH_2$, and ^{13}CH interferences [1].

Experimental Arrangement

The ECR ion source, shown in Figure 2, is a variation on other ECR source designs. Featuring a single ended plasma bottle, and miniaturised magnet arrangement so as to reduce the plasma bottle volume. This was done to maximise the efficiency of the source, as the only paths for gas to be removed from the plasma bottle is via beam extraction as an ion, or by pumping which is restricted by the low conductance of the extraction aperture.

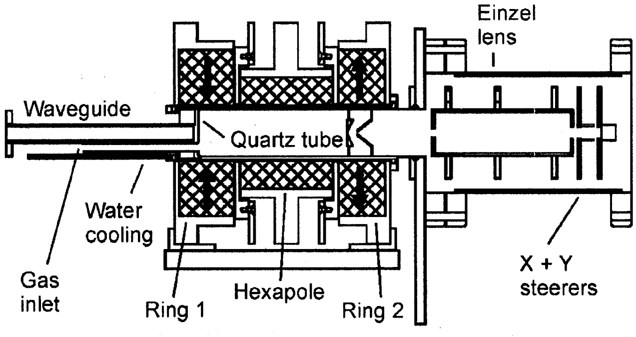

Figure 2: Schematic of the ECR ion source. Parts of the internal and external support structures are not shown.

Sample gases are introduced to the ions source via the gas inlet indicated in figure 2. This is fed by 2 capillary lines of 25µm internal diameter. One line delivers the sample gas/vapour, and the other delivers a support gas (if required -- typically helium).

Static pressures of sample and support gas are placed on the inlet side of the capillaries typically in the order of hundreds of Torr, so that the transition between lamina and molecular flow can occur within the capillary preventing fractionation effects.

Molecular Interference with Water

When water vapour is introduced to the system via a capillary line, the H_2O molecule is first ionised to the 1+ charge state within the ECR region of the source. Further bombardment of the molecule by energetic electrons results in the molecule breaking up as it cannot maintain a 2+ charge state. This results in the generation of a free hydrogen atom, and an OH molecule. Following a similar process the OH will be broken into its single constituent, a hydrogen and oxygen atom.

The oxygen free of the parent water molecule can continue to be stripped to higher charge states by further electron bombardment in the ECR region. When extracted the oxygen atom maybe at a charge state ranging from 1+ to 8+. The extracted beam can then be analysed for example in the 2+ charge state meaning that the $^{16}O^{2+}$, $^{17}O^{2+}$, and $^{18}O^{2+}$ will now appear at the m/q values 8, 8.5, and 9. As the H_2O and OH molecule can't maintain a 2+ charge state these values are free of molecular interference.

Figure 3 shows an example water vapour scan. The 2+ charge state has been shifted and expanded to line up with the 1+ charge states of the oxygen isotopes at mass 16, 17, and 18 to show the removal of molecular interference at the 2+ charge state.

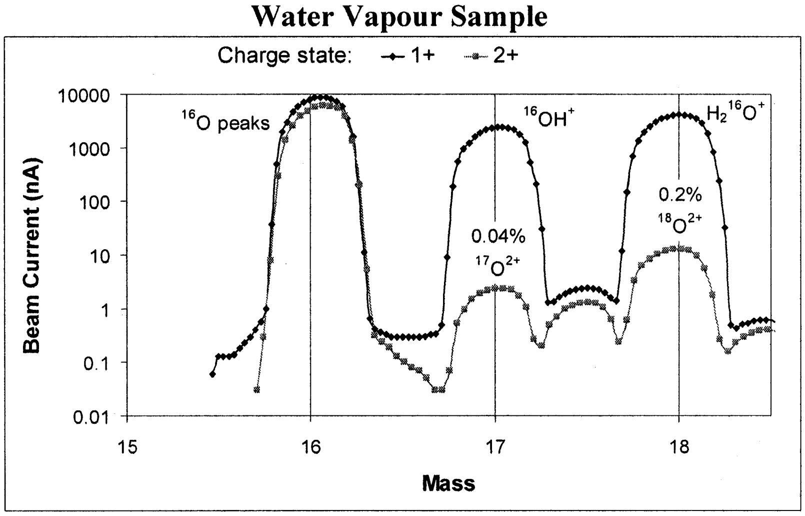

Figure 3: The above shows the 1+ and 2+ ion peaks for oxygen overlaid. In the 1+ charge state, the rare isotopes are obscured by molecular ions while in the 2+ charge state they are free from interference.

Working with High Charge States

The developed ECR ion source is effective at generating a range of charge state ions. This can be scene in Figure 4, which is the mass scan of argon. The scan also indicates the presence of background hydrogen, oxygen, nitrogen and carbon within the scan, due to residual gases in the vacuum system. Many of the low intensity peaks with m/q 24 and greater can be attributed to various molecular species formed from H, C, N and O, such as hydrocarbons, CO, NO, O_2, N_2, etc.

Although the production of higher charge states is useful for the generation of alternative charge states free of molecular interference, it does introduce the occurrence of other form of interferences. There are 2 main forms of interference that can be observed in our results of the current experimental IRMS instrument.

Firstly, similar or identical m/q values can result from different charge states of atomic ions formed from a number of elements and their isotopes. The most apparent point where this occurs is at m/q of 4 which can contain contributors such as $^{12}C^{3+}$, $^{16}O^{4+}$, $^{40}Ar^{10+}$, $^{36}Ar^{9+}$, $^{20}Ne^{5+}$ and $^{4}He^{+}$. This can be seen in Figure 4 at m/q value of 4, and another such interference at m/q of 18 where H_2O^+ coincides with $^{36}Ar^{2+}$.

was extracted at the 2+ charge state, shifting the apparent m/q value to 80. Peak B, is the result of $^{40}Ar^{3+}$ changing to $^{40}Ar^{1+}$ giving it an apparent m/q value of 120. The peak at m/q = 30 is a further example, due to the $^{40}Ar^{3+}$ to $^{40}Ar^{2+}$ charge change. These peaks show a distorted peak shape as the charge change may occur very close to or within the extraction region.

Potential interferences from charge changing events can be overcome by the addition of and Electro-Static Analyser (ESA) to eliminate ions of incorrect energy to charge ratios.

References

M.A.C. Hotchkis and T. Wei, Radiocarbon detection by ion charge exchange mass spectrometry, Nucl. Instr. & Meth. B 259 (2007) 158.

M.A.C. Hotchkis and C.L. Waring, An Isotope Ratio Mass Spectrometer and Methods for Determining Isotope Ratios, Australian Patent Application No. PCT/AU2006/001284.

Equation 1:

$$\left.\frac{m}{q}\right._{Apparent} = \frac{m q_i}{q_f^2}$$

Where;
m = Mass
q_i = Initial Charge
q_f = Final Charge

Secondly, charge changing events can occur. This is where a higher charge state ion can recapture 1 or more electrons after extraction. The resulting peak does not appear at the correct m/q value, but takes on an apparent value higher up the spectrum due to the additional energy. The apparent value can be calculated as using Equation 1.

Figure 4 shows 2 peaks labelled A and B which are the result of charge changing. Peak A corresponds with $^{40}Ar^{2+}$ changing to $^{40}Ar^{1+}$. Thus the resulting ion has an energy f 30keV due to the 15kV extraction voltage when in the ion

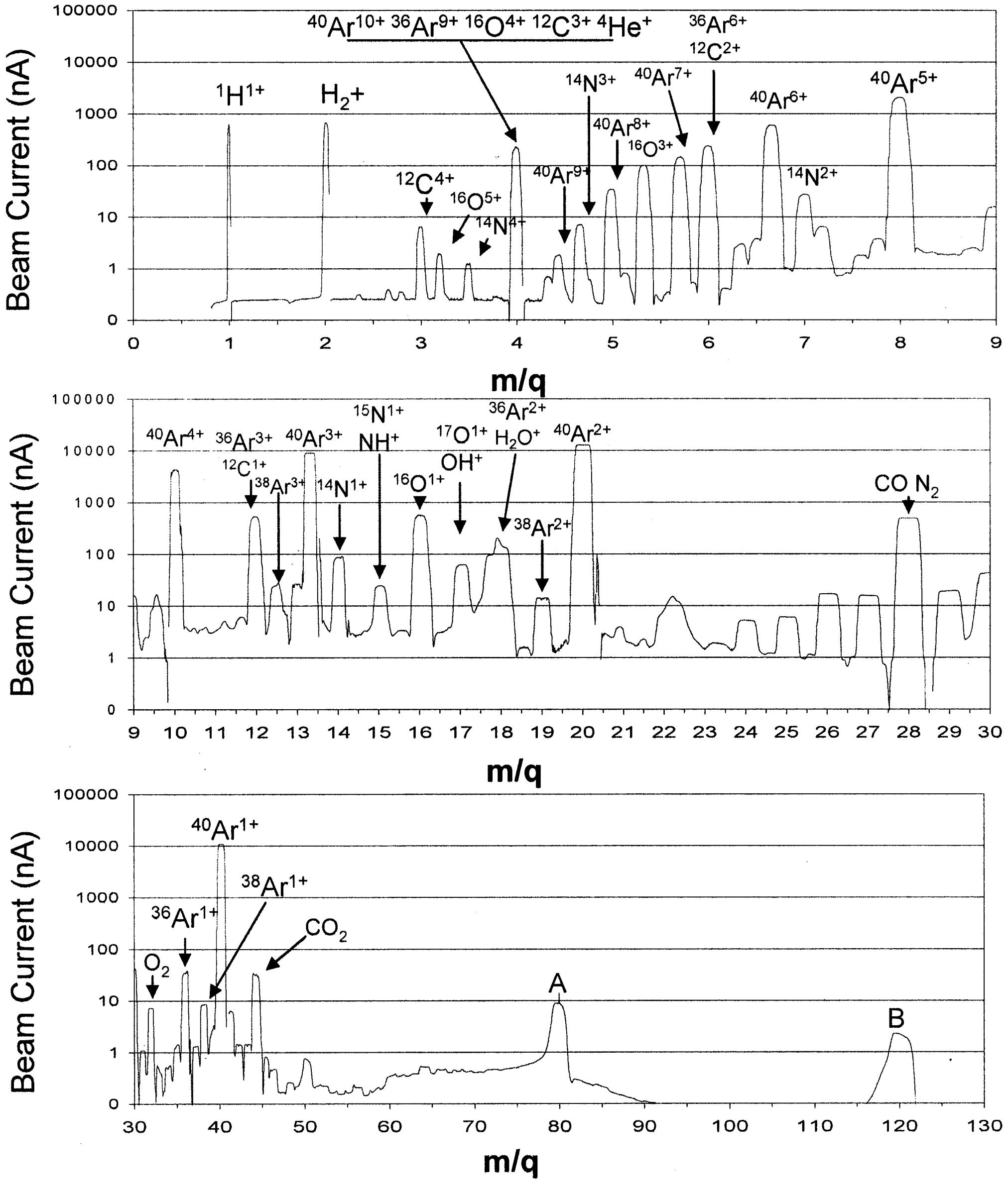

Figure 4: The above are a mass spectrum of Argon gas spit into three sections.