Mass Spectrometry with an ECR Ion Source

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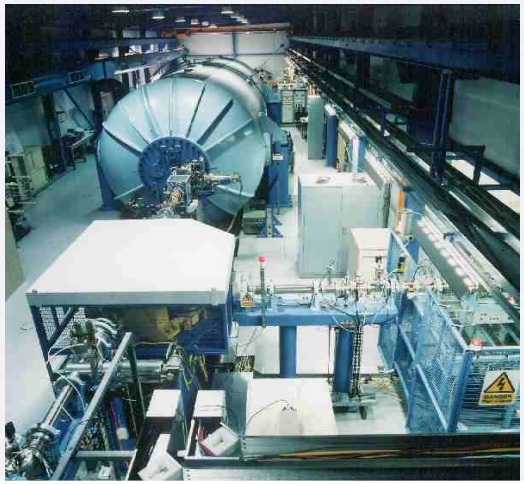
Topics:

- Mass Spectrometry with multiply charged ions
- Applications
- ECR ion source – suitability for mass spec?
- Current progress

Mass Spectrometry with multiply charged ions

- Accelerator Mass Spectrometry (AMS)
  - normally uses negative ions, with charge exchange to multiply-charged positive ions in Tandem accelerator
- **Radiocarbon analysis using ion charge exchange mass spectrometry (ICE-MS) – two different versions**
- AMS with ECR ion sources (mainly Argonne Nat Lab – paper by Richard Pardo at this meeting)
- **Isotope ratio mass spectrometry (stable isotopes)**

ANTARES tandem accelerator at ANSTO



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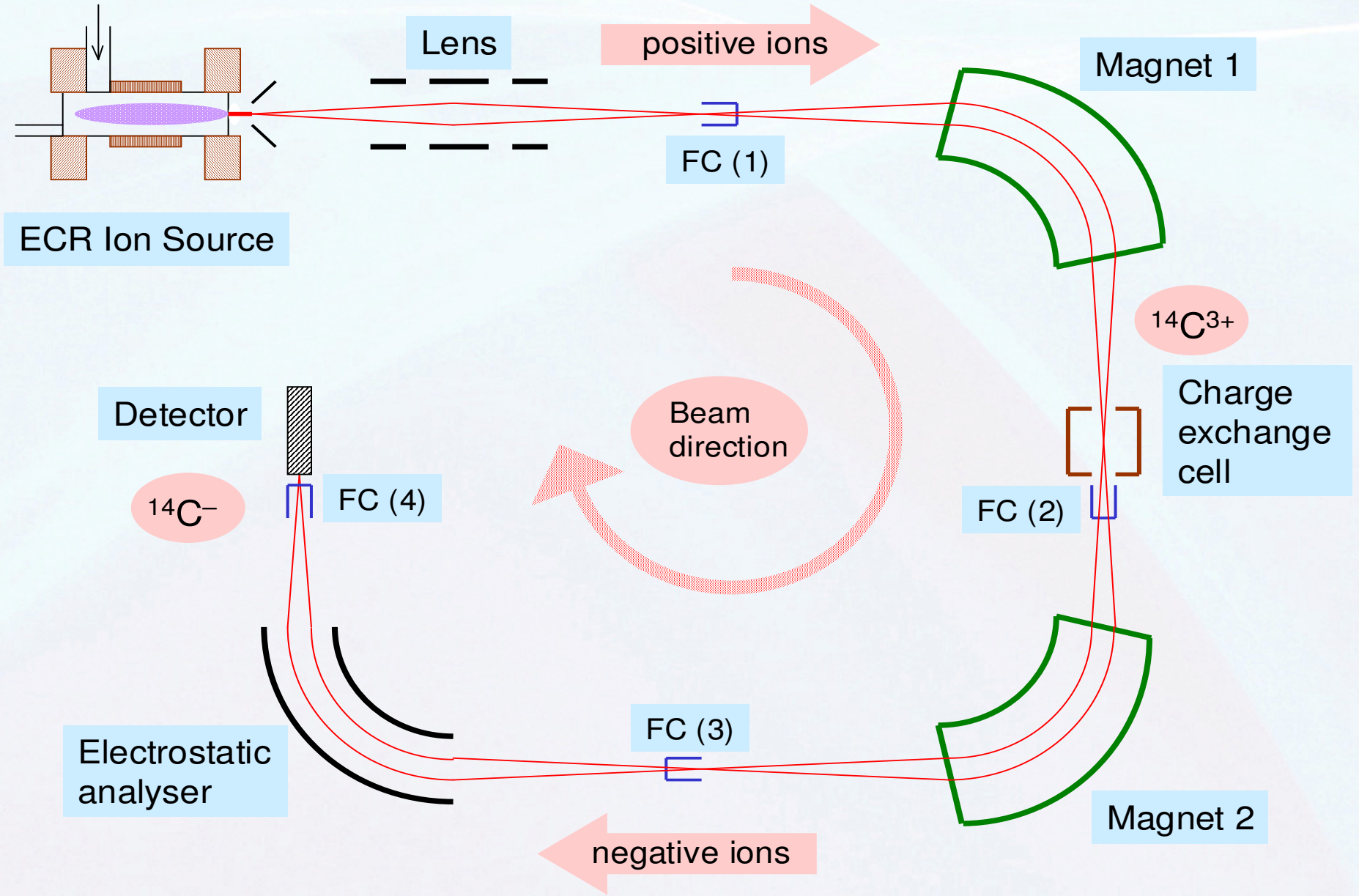
Ion Charge Exchange Mass Spectrometry

A method for measuring radiocarbon (^{14}C) at low levels
[like AMS, but in reverse]:

- produce highly charged carbon ions ($q \geq 2$)
  – *eliminate molecular ions like ^{13}CH, $^{12}CH_2$*
- convert to negative ions in a charge exchange cell
  – *eliminate nitrogen ^{14}N*
- leaves pure ^{14}C beam! (in theory)



ICE-MS

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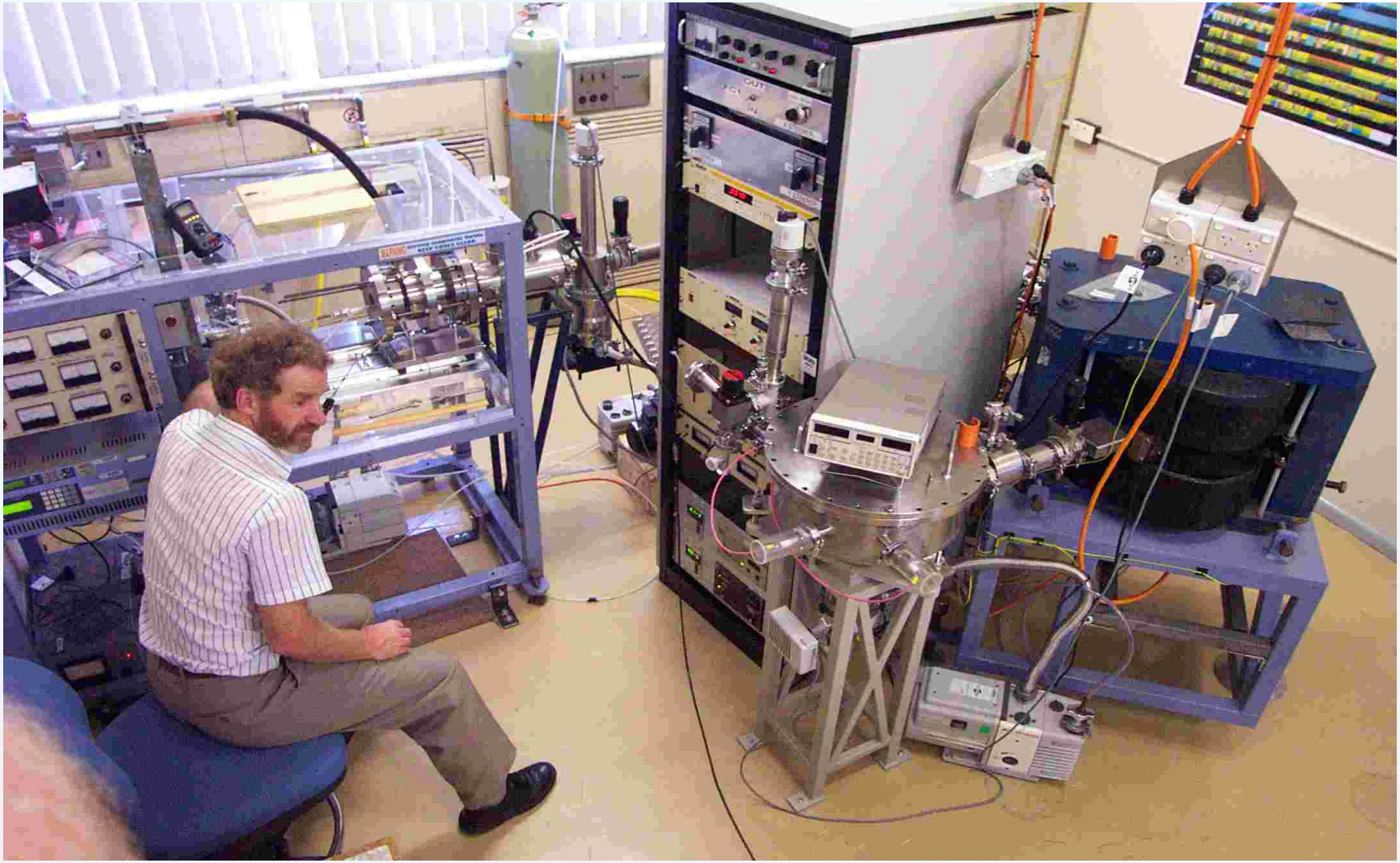

M.A.C. Hotchkis and T. Wei, Nucl. Instr. & Meth. B 2007, 259: 158-164.

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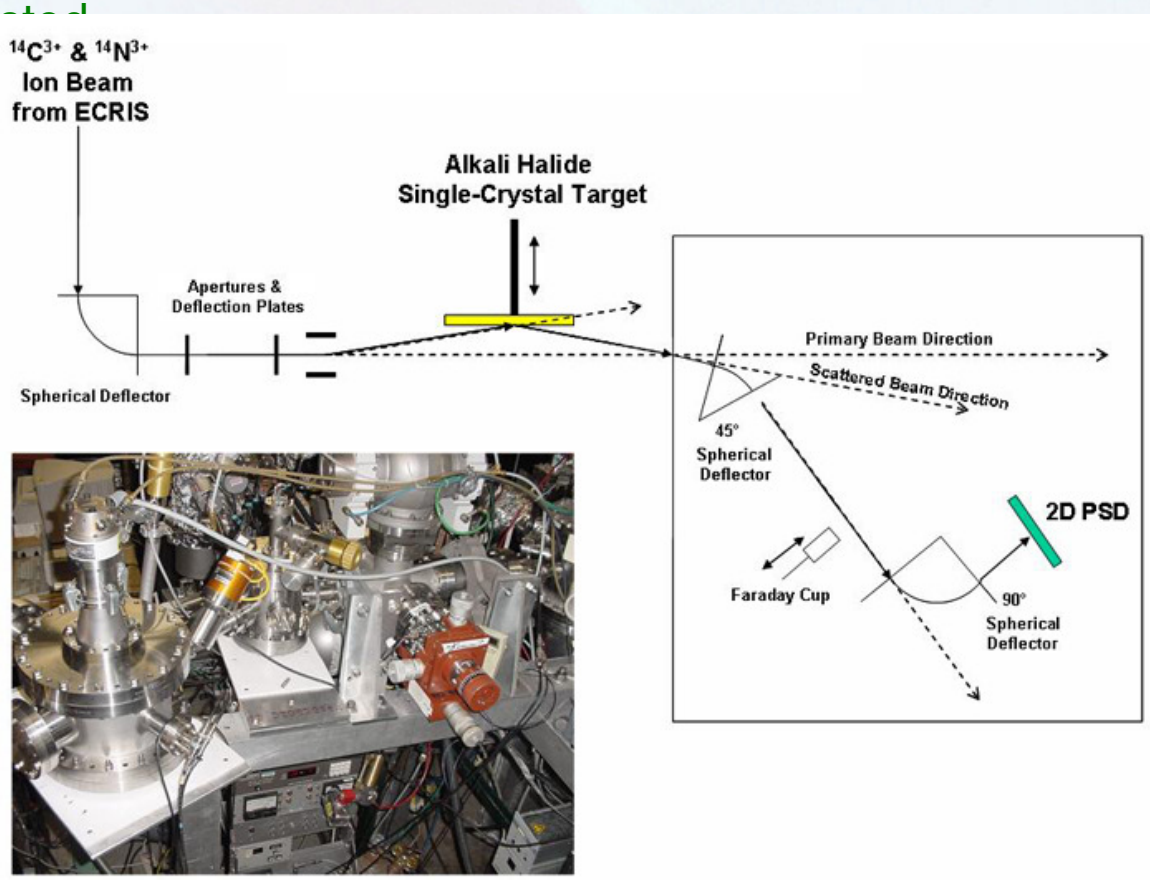
Ion Charge Exchange Mass Spectrometry

The idea has a longish history:

- R Middleton 1978 – Rochester Conference on Radiocarbon Dating with Accelerators: first sugg
- RB Schubank 1999 – AMS source, but not built
- Fred Meyer (2002) – US Patent 6455844: use of charge exchange on a surface

F. W. Meyer E. Galutschek, M. Hotchkis, AIP Conference Proceedings Vol 1099 (1), 308-313 (2009).



Ion Charge Exchange Mass Spectrometry

ANSTO

System performance:

- gas consumption rate: 4ng/s (CO_2)
- overall ion source efficiency 30-50%
- charge exchange efficiency ~10% ($3+ \rightarrow 1-$)
- achieved isotopic ratio sensitivity $^{14}C/^{12}C$ 10^{-9}
- sensitivity: a few μBq ^{14}C – *ideal for biomedical applications*

Scope for improvement in sensitivity with charge state separator, additional ESA, improved charge exchange cell design

M.A.C. Hotchkis and T. Wei, Nucl. Instr. & Meth. B 2007, 259: 158-164.

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Mass Spectrometry with multiply charged ions

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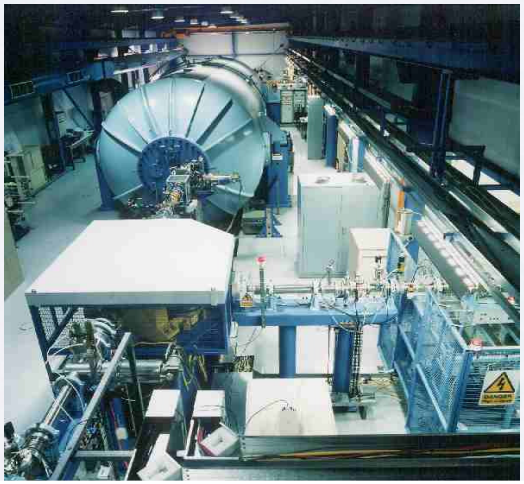

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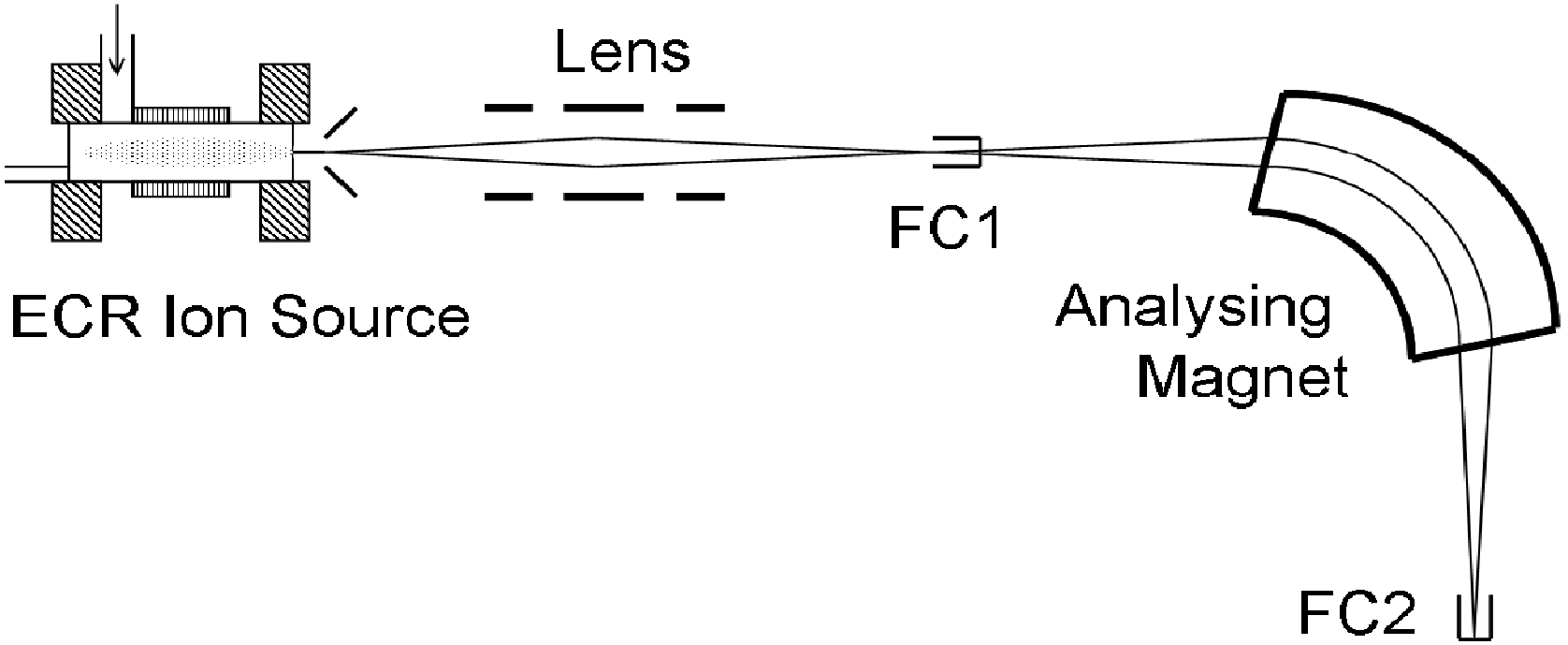
Kidera et al. at RIKEN

Ar, Kr and Xe isotopic analysis examined using RIKEN ECR ion source
(Kidera M, Takahashi K, Enomoto S, Mitsubori Y, Goto A, Yano Y. Eur. J. Mass Spectrom. 2007; 13: 239)

Elemental analysis – paper at this meeting on new system; also earlier work with RIKEN ECRIS



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" IRMS++ "

As ICE-MS but first stage only:

- inject sample as gas or vapour
- use multiply charged atomic ions – *eliminate molecular ions*

M.A.C. Hotchkis, D. Button and C.L. Waring, Rapid Comm. Mass Spectrom. 2008, 22: 1408-1414.

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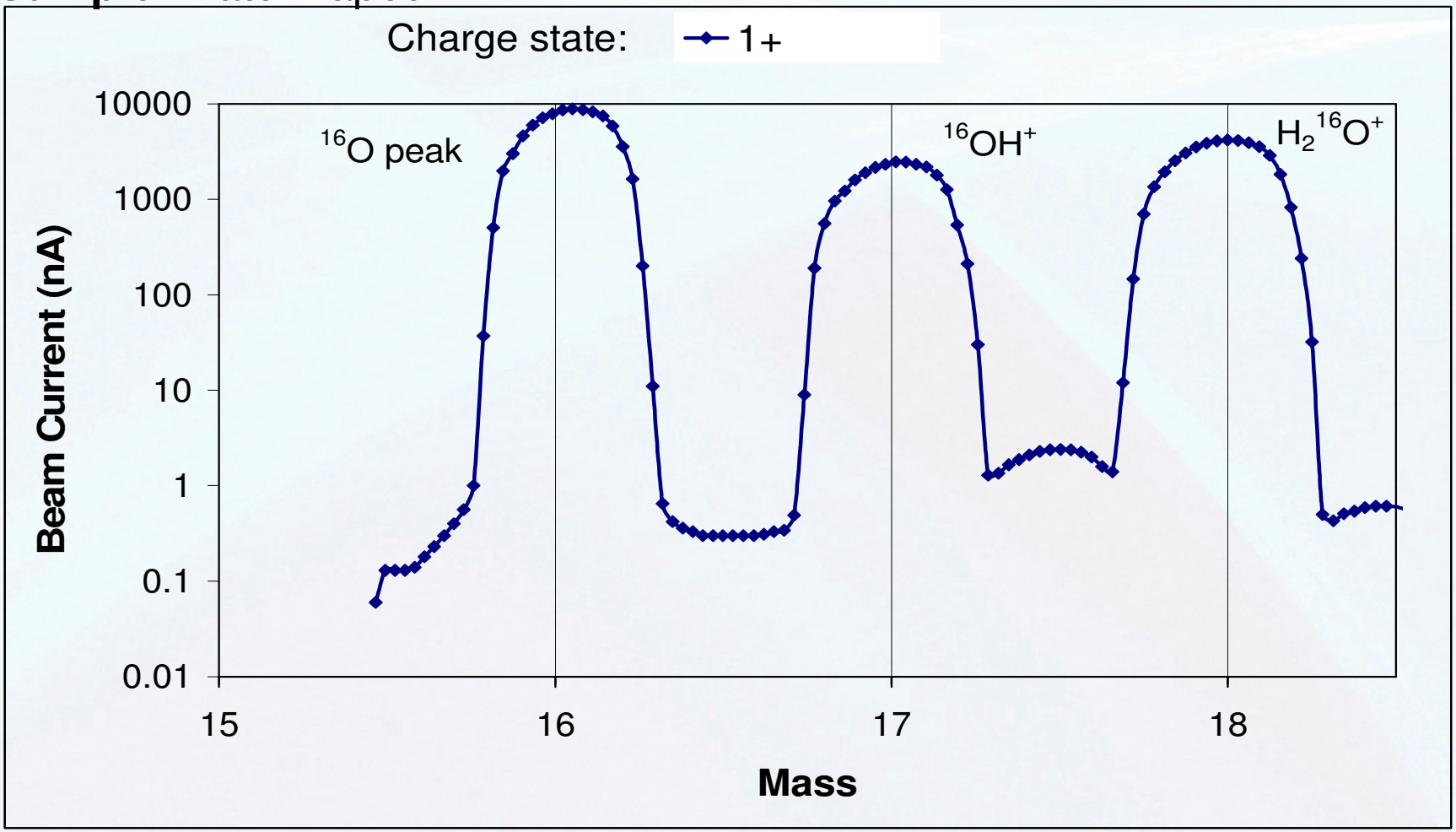
Sample: water vapour



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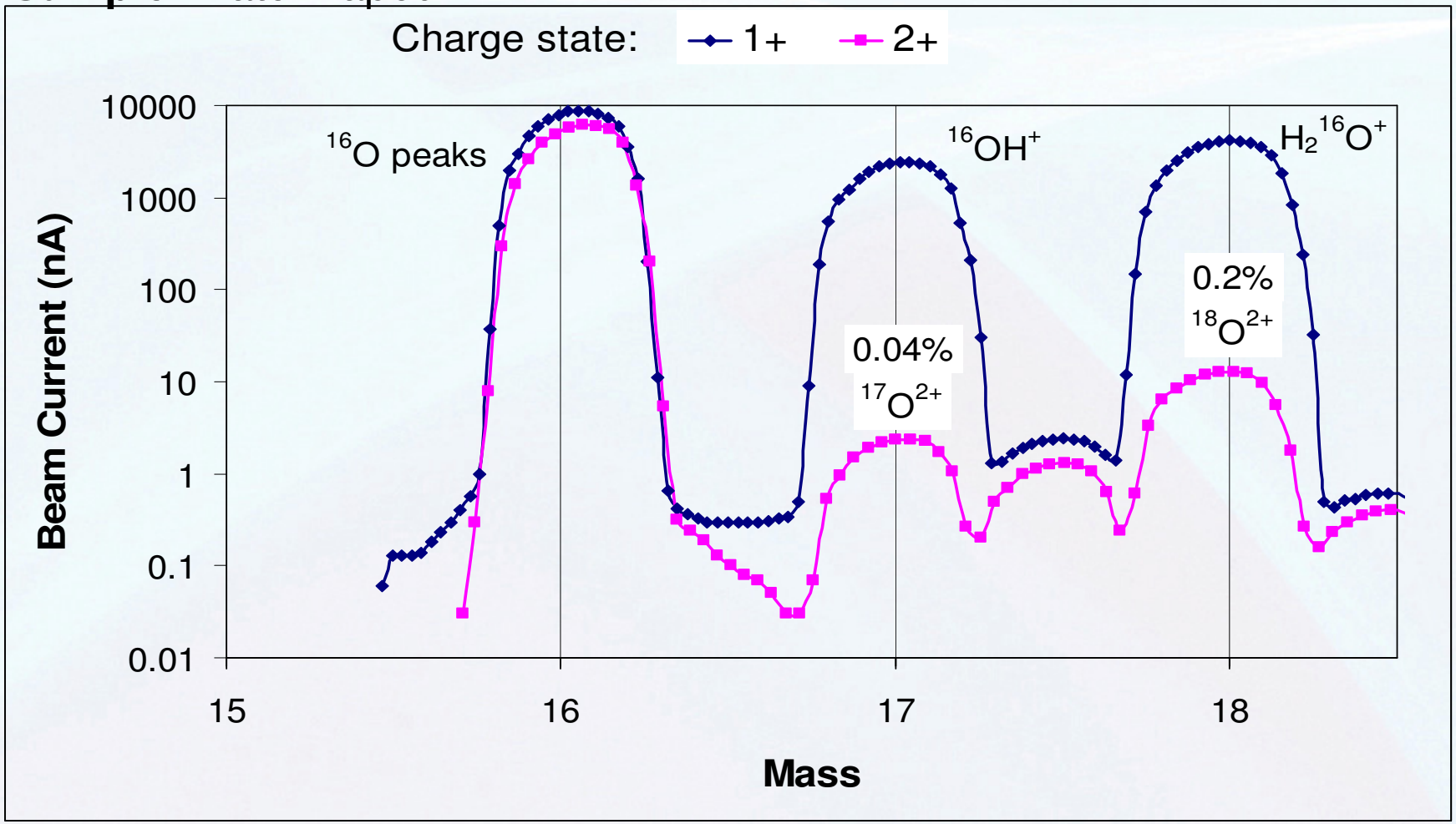

- 2+ ions appear to be best hence IRMS++
- tested on C, N and O isotopic ratios

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ANSTO ECR Ion Source

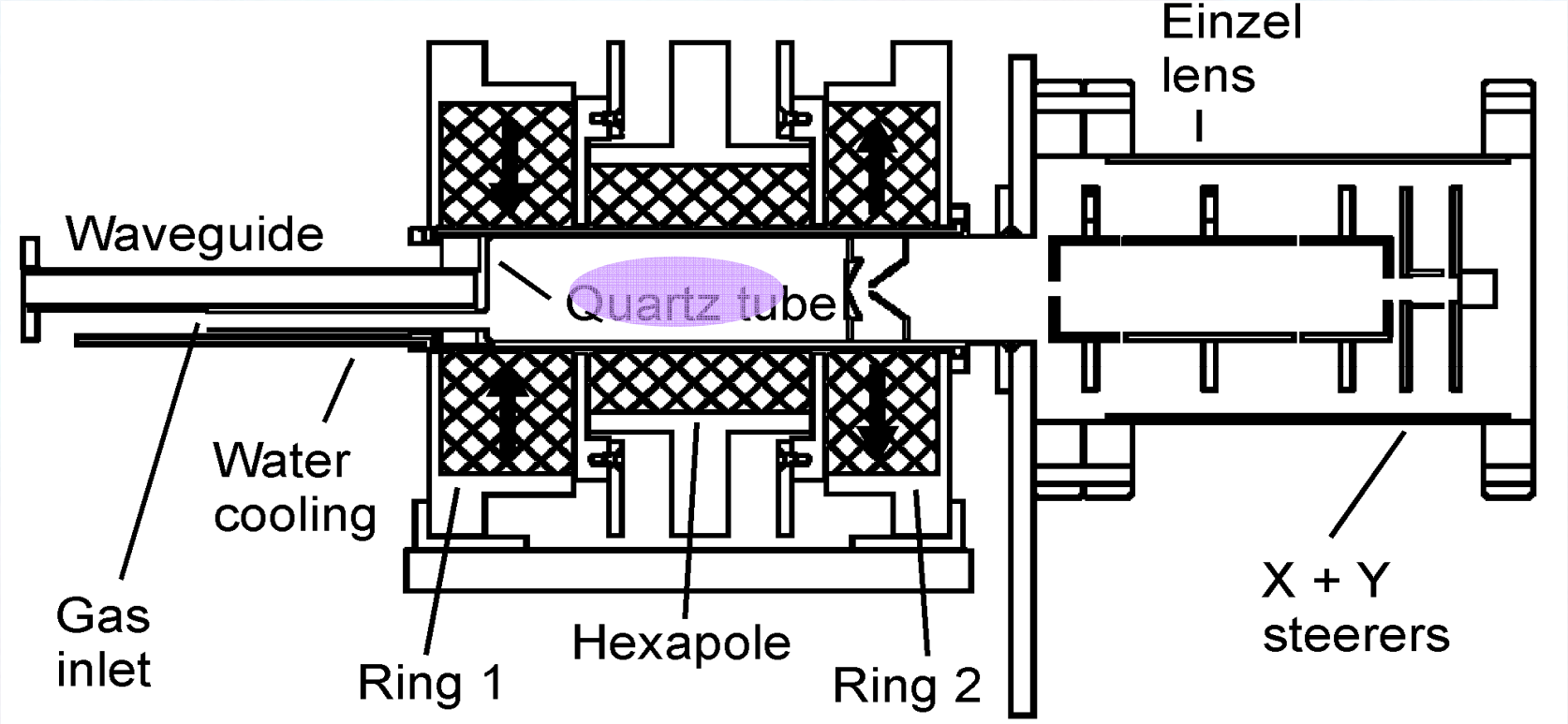
- 7GHz up to 100W
- permanent magnets: 2 rings and hexapole, N42
- quartz plasma chamber

Electron cyclotron resonance:

angular frequency $\omega_c = \frac{eB}{m}$

$\Rightarrow$ $f_c = 28 \times B$

GHz Tesla



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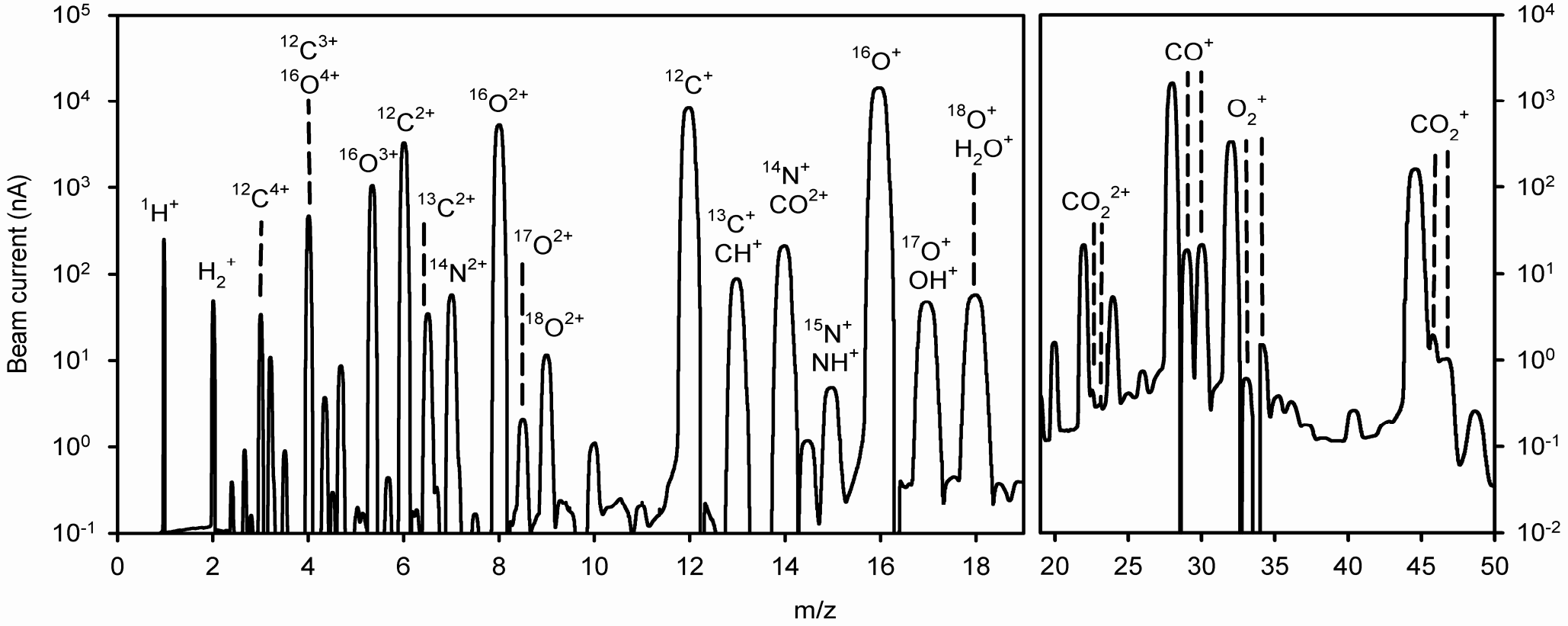
Sample: carbon dioxide



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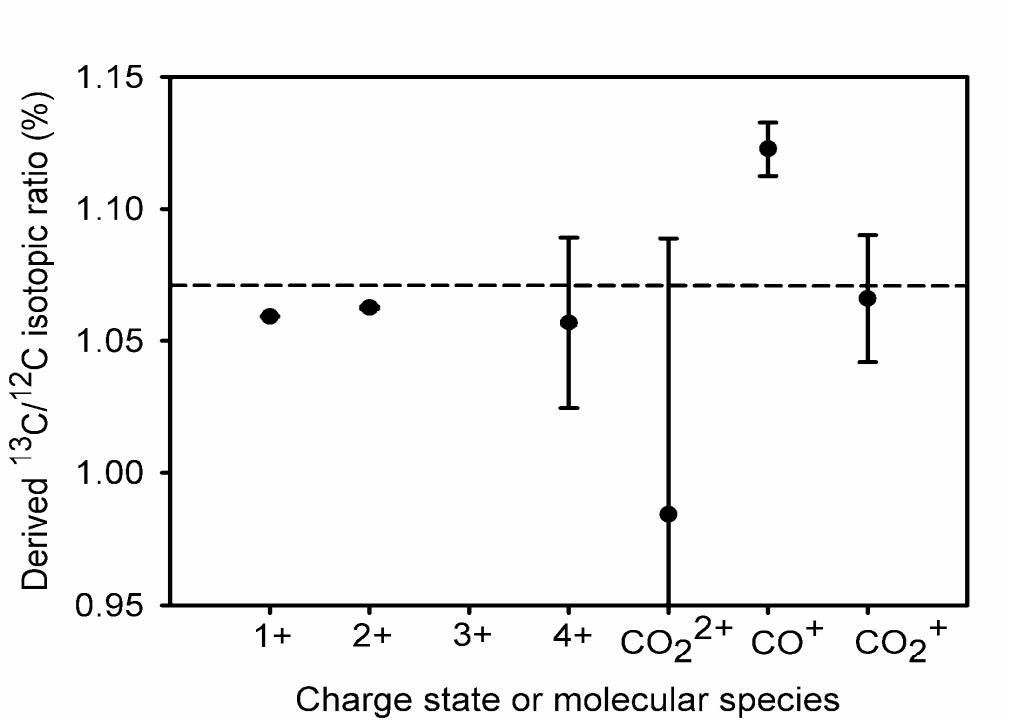
Sample: carbon dioxide

Ion species	Derived 17/16 ratio (%)	Derived 18/16 ratio (%)
O^+	0.3336 ± 0.0003	0.4029 ± 0.0003
O^{2+}	0.0370 ± 0.0004	0.2137 ± 0.0005
O^{3+}	0.0372 ± 0.0008	312.5 ± 0.0012
O^{4+}	0.0364 ± 0.0038	0.2118 ± 0.0044
O^{5+}	<0.12	0.2630 ± 0.0832
CO^+	—	1.3290 ± 0.0037
O_2^+	0.0775 ± 0.0025	0.1965 ± 0.0052
CO_2^+	—	0.3009 ± 0.0035

- check of accuracy (not precision)
- identify most suitable charge state

Sample: carbon dioxide



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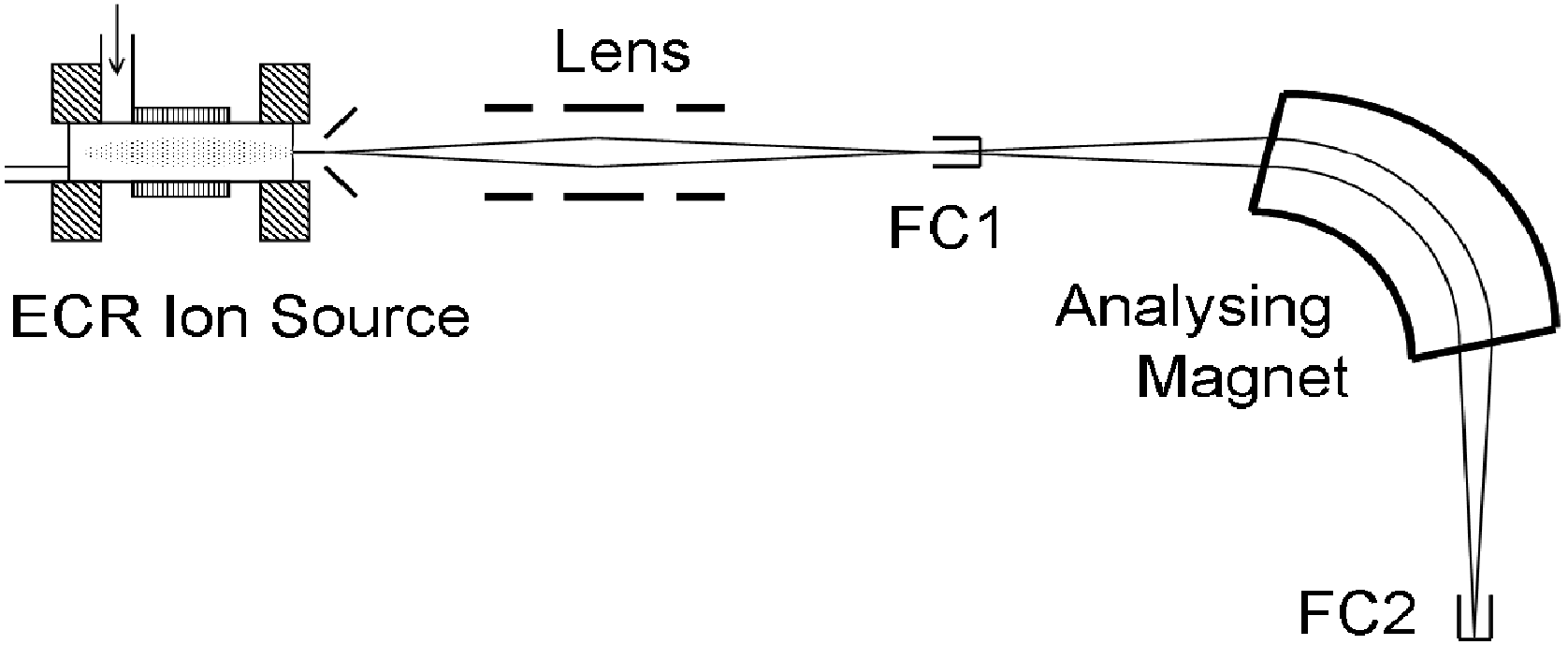
Nitrobenzene = $C_6H_5NO_2$

	Beam current (nA)	Mass / charge ratio	Ions	Measured ratio	Expected ratio
1+	1650	12	$^{12}C^+$		
	33.6	13	$^{13}C^+$, CH^+	2.0%	1.112%
	1578	14	$^{14}N^+$		
	216	15	$^{15}N^+$, NH^+	13.7%	0.367%
	11420	16	$^{16}O^+$		
	4570	17	$^{17}O^+$, OH^+	40.0%	0.038%
	9100	18	$^{18}O^+$, H_2O^+	79.7%	0.200%
2+	477	6	$^{12}C^{2+}$		
	5.7	6.5	$^{13}C^{2+}$	1.195%	1.112%
	480	7	$^{14}N^{2+}$		
	1.76	7.5	$^{15}N^{2+}$	0.367%	0.367%
	3710	8	$^{16}O^{2+}$		
	2.74	8.5	$^{17}O^{2+}$	0.074%	0.038%
	8.3	9	$^{18}O^{2+}$	0.224%	0.200%



Advantages:

- direct measurements possible on gases
  or vapours such as water, carbon dioxide, organics, etc
- small sample capability (due to high efficiency ion source) ⇒ critical in many applications, eg ice cores, speleothems, soil moisture, solar wind, stratospheric air
- ^{17}O easy to measure

but there are problems…..

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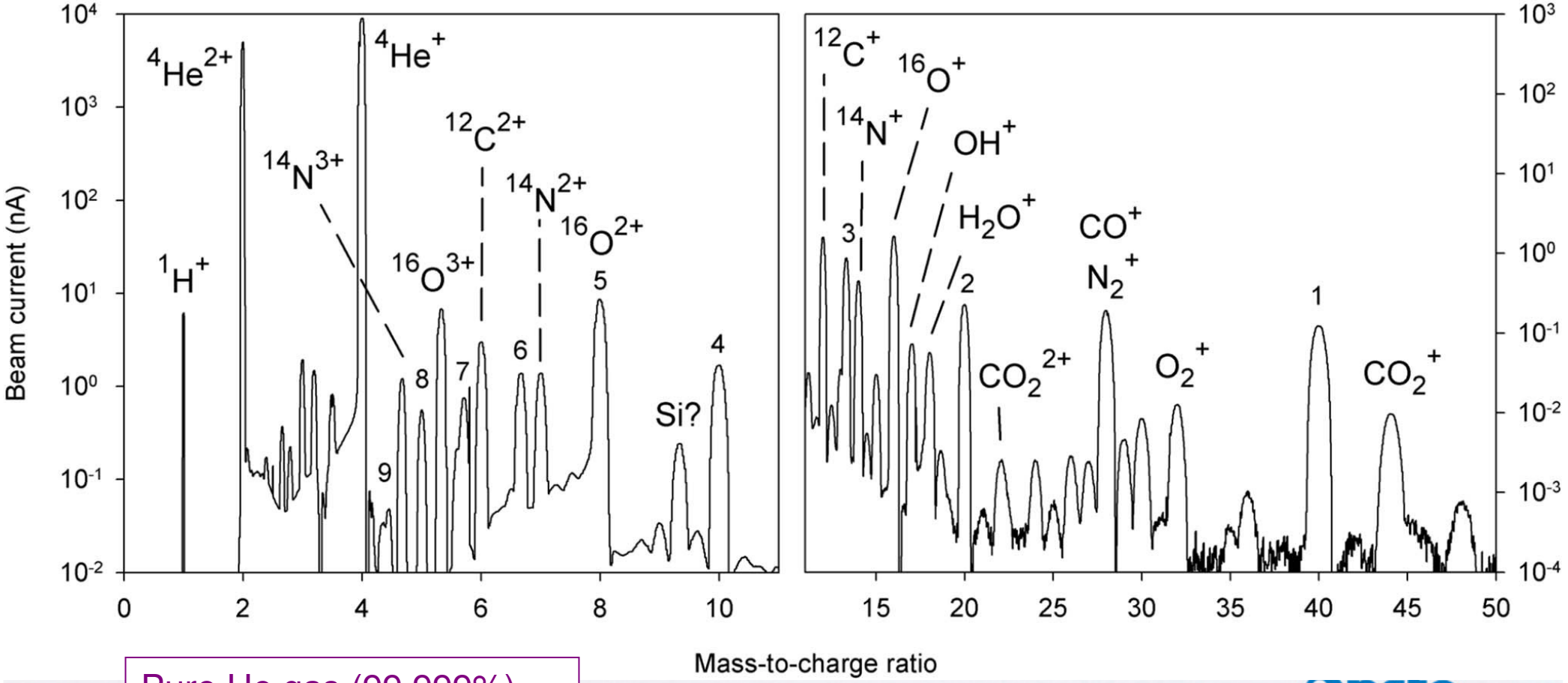
ECR ion source issues:

- backgrounds / contamination
- absorption / desorption effects, long time constants



Pure He gas (99.999%)

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Hotchkis M, Buckley D, Button D. Rev. Sci. Instrum. 2008; 79: 02A304..

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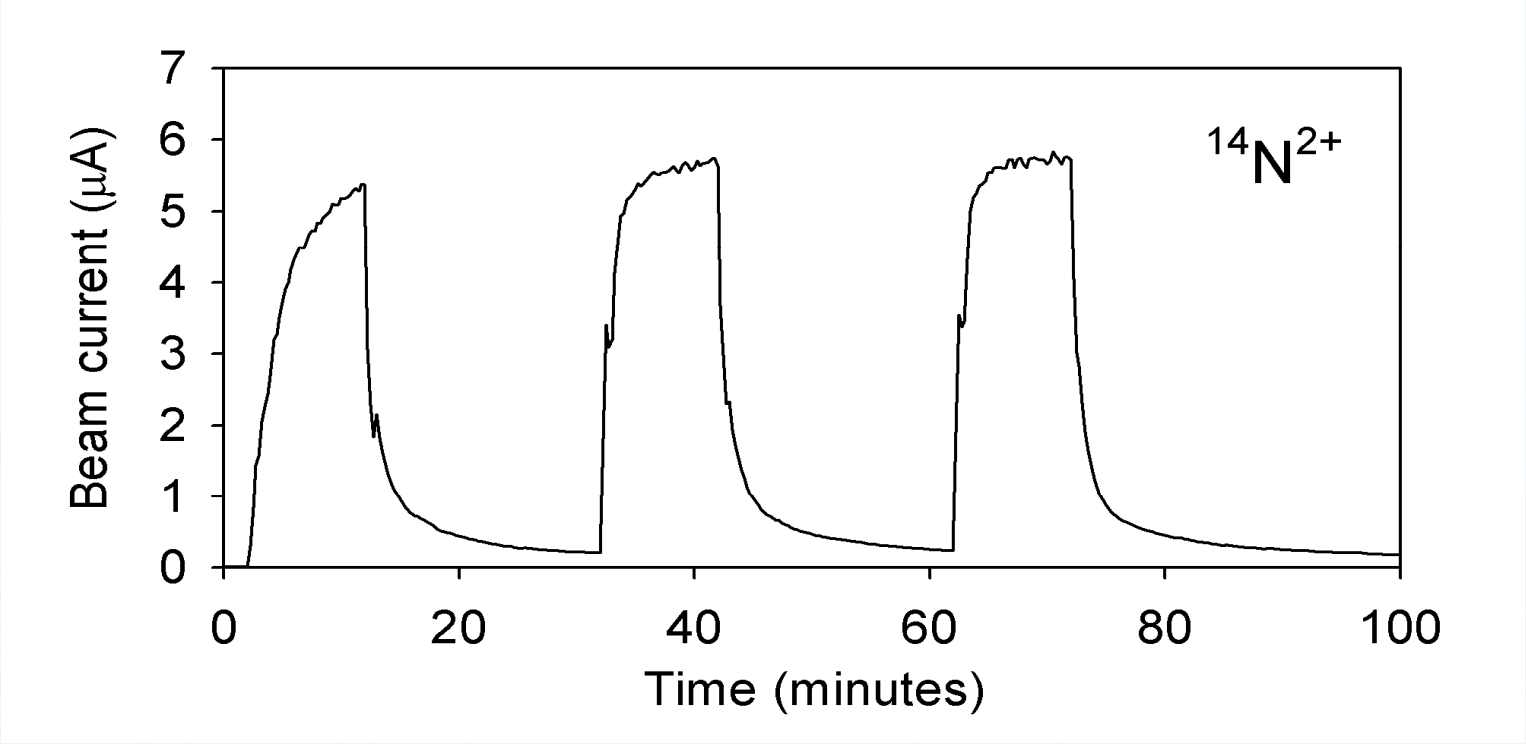

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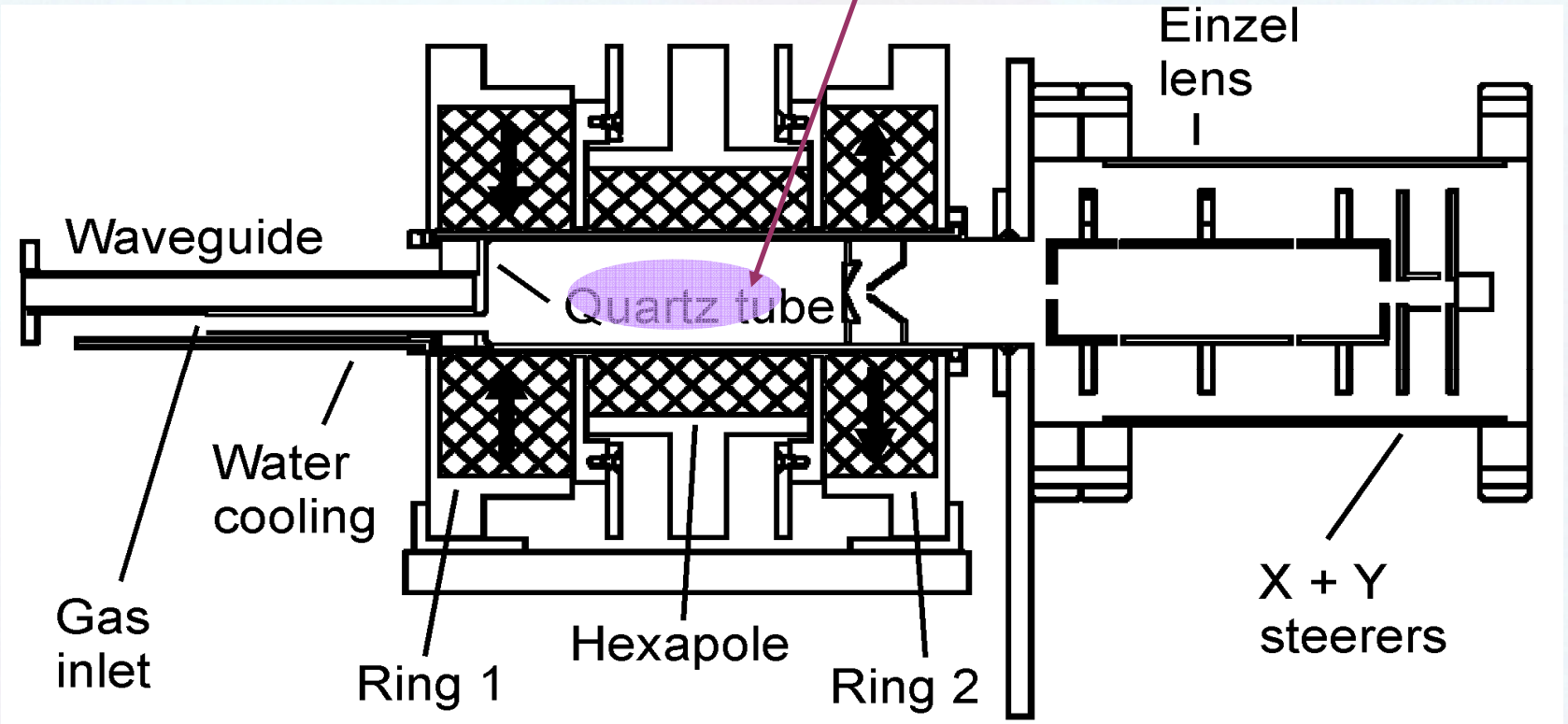
ECR ion source issues:

N_2 is non-reactive **but** the plasma is full of **active** species:
N^*, N^+, N^{2+}, etc



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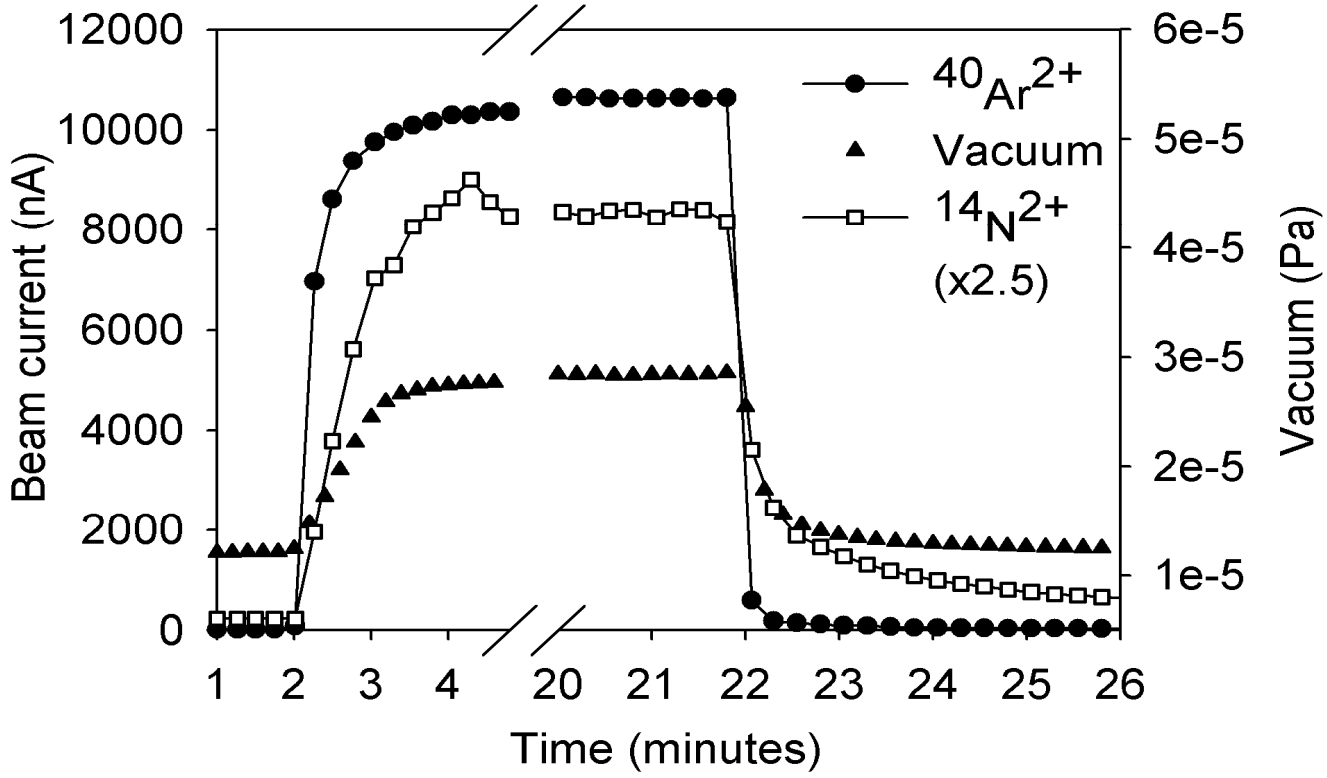
ECR ion source issues:

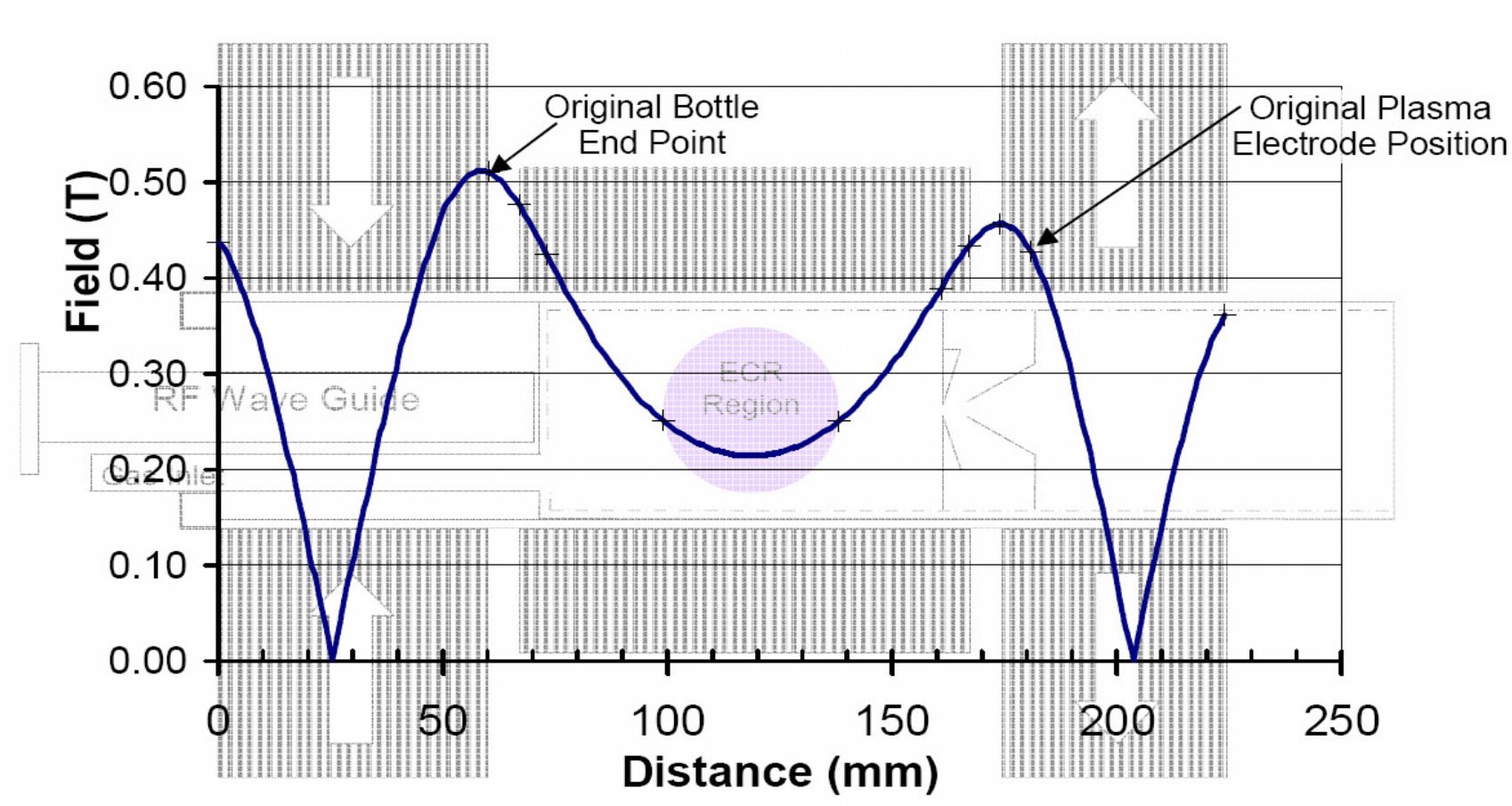
- correlated with external vacuum measurement
- no delay to vacuum reading if plasma turned off

Minimal effects for noble gases – not a pumping speed effect but a 'chemical' reactivity effect



ECR ion source issues:

- effect of shortening the plasma chamber



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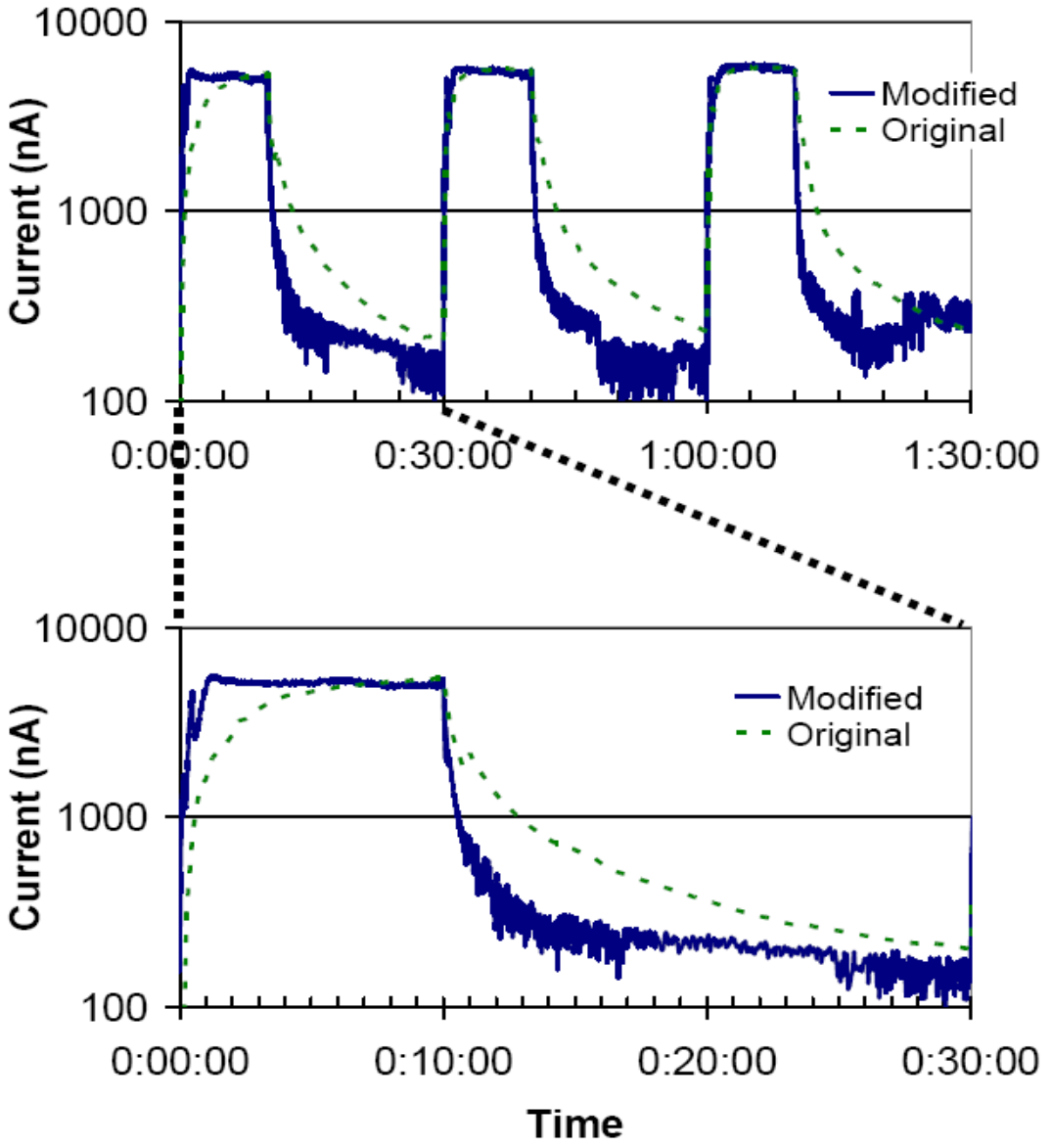
ECR ion source issues:

- effect of shortening the plasma chamber
- minimizes the surface area



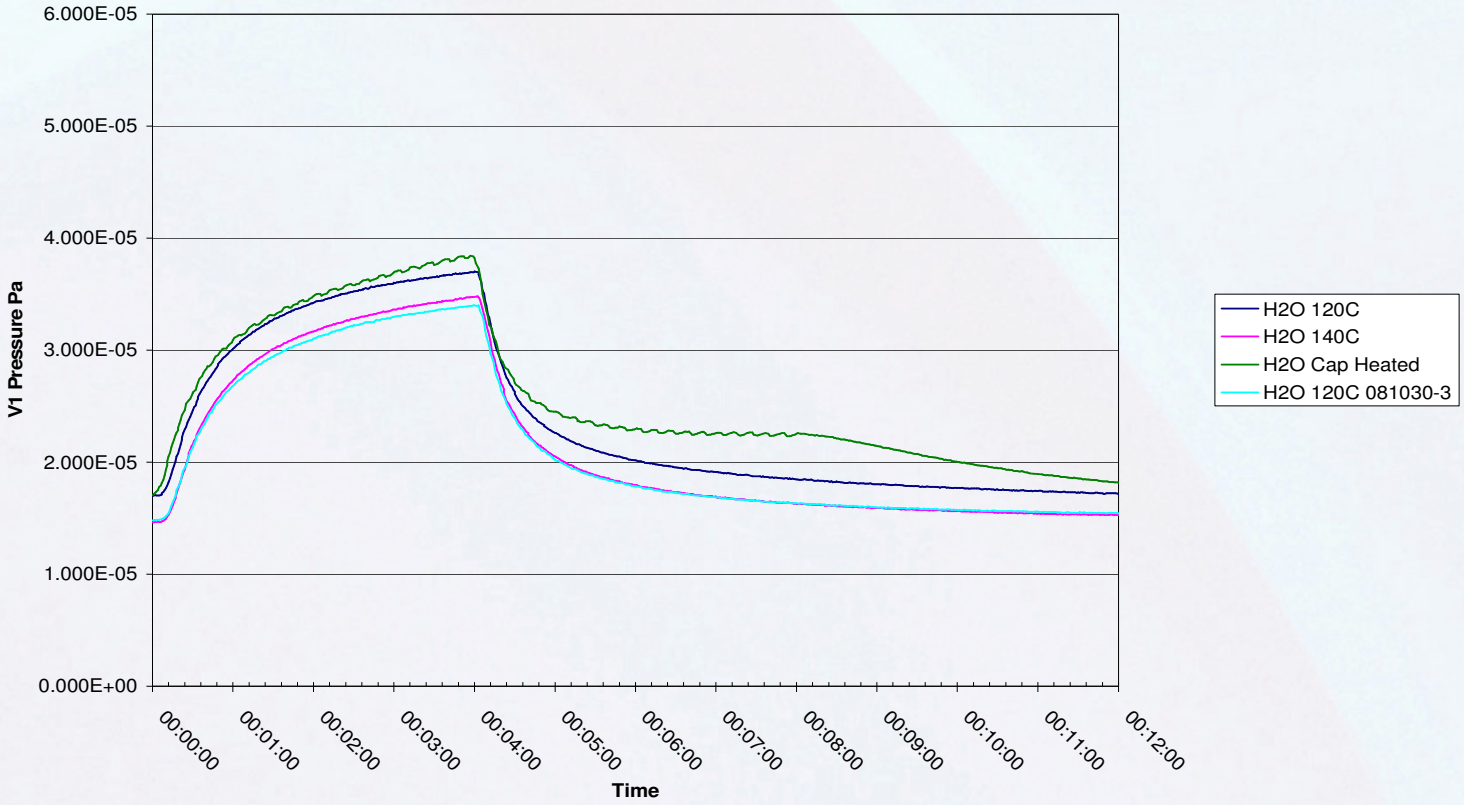
ECR ion source issues:

Also tried various cleaning procedures

- oxygen or water vapour plasma to remove carbon
- hydrogen to remove oxygen

Problems persist…

Water vapour injections



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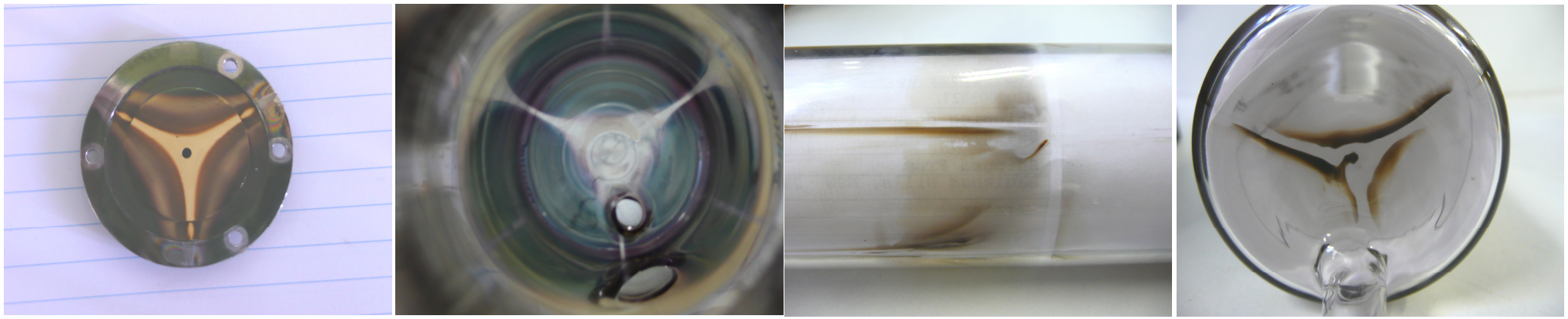
ECR ion source issues:

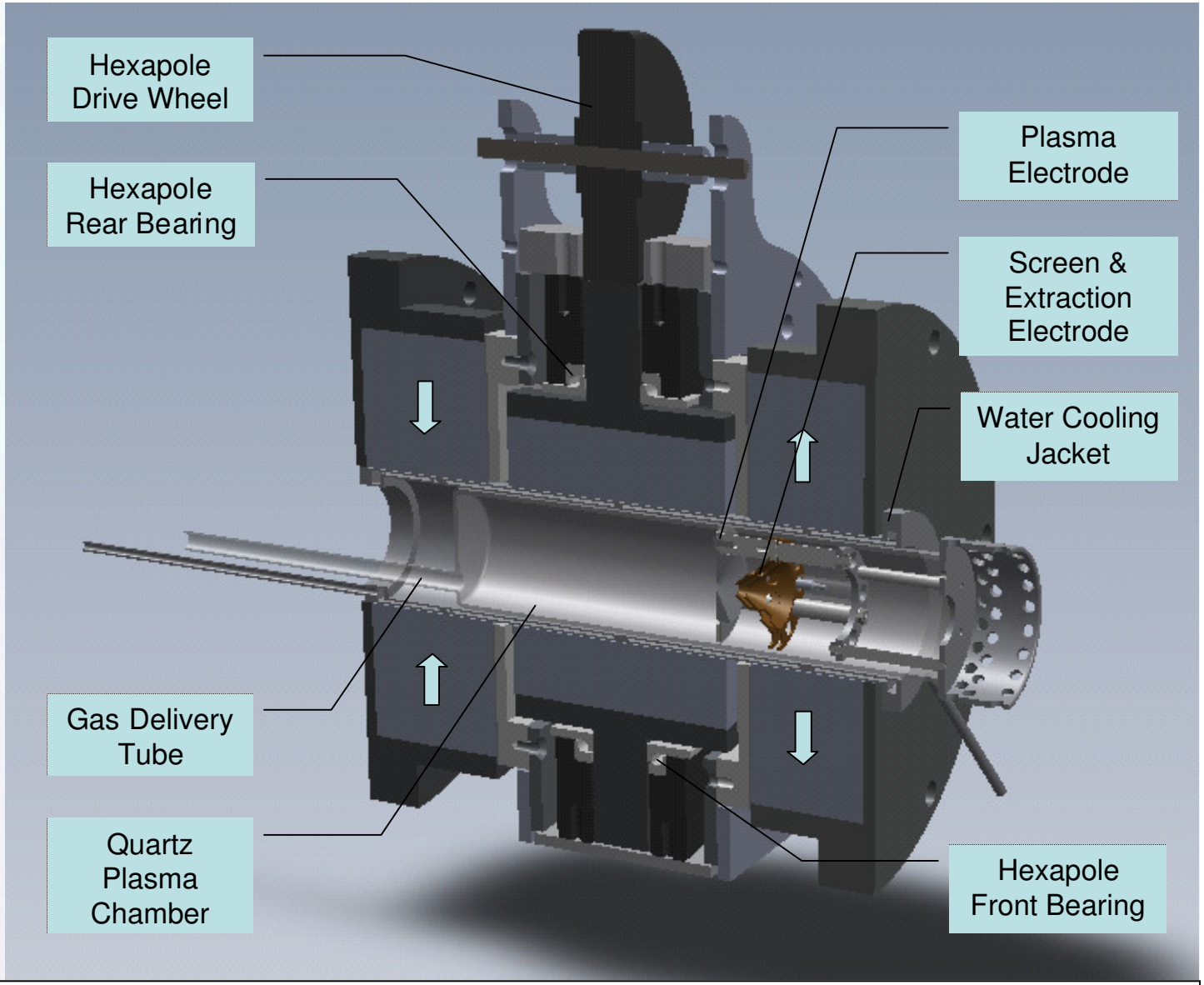
- tell-tale marks
- need to rotate hexapole to clean the inner surface of plasma chamber uniformly



Quartz tube and plasma electrode after running cyclohexane

ECR ion source issues:

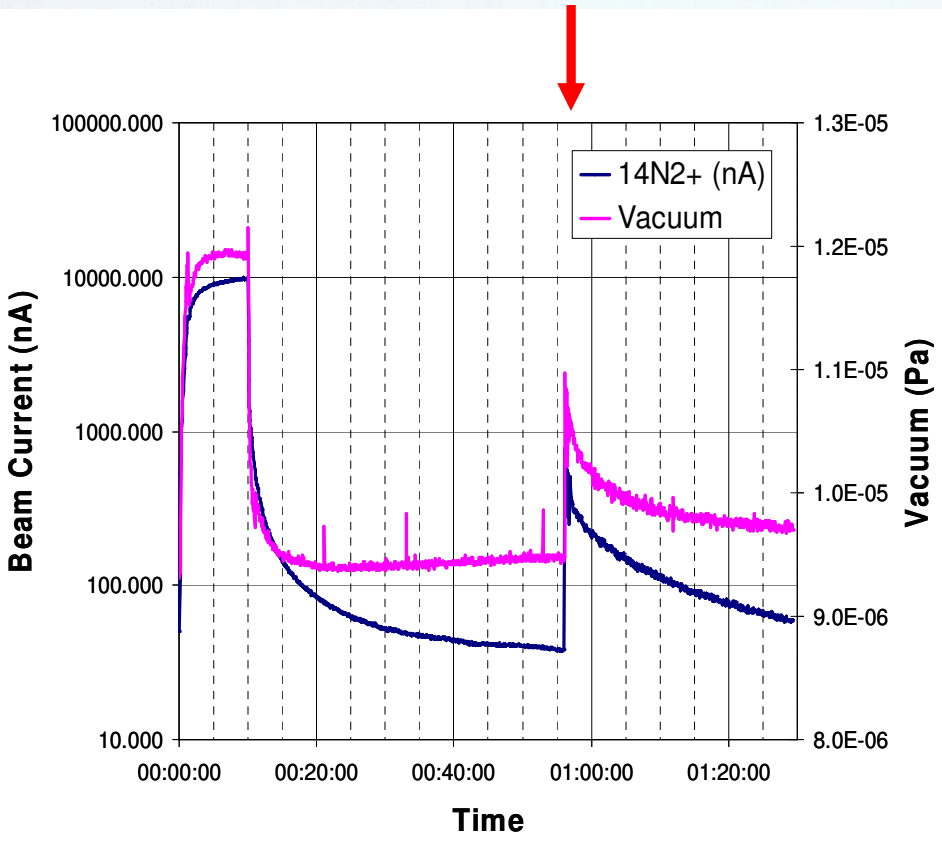
Rotating hexapole



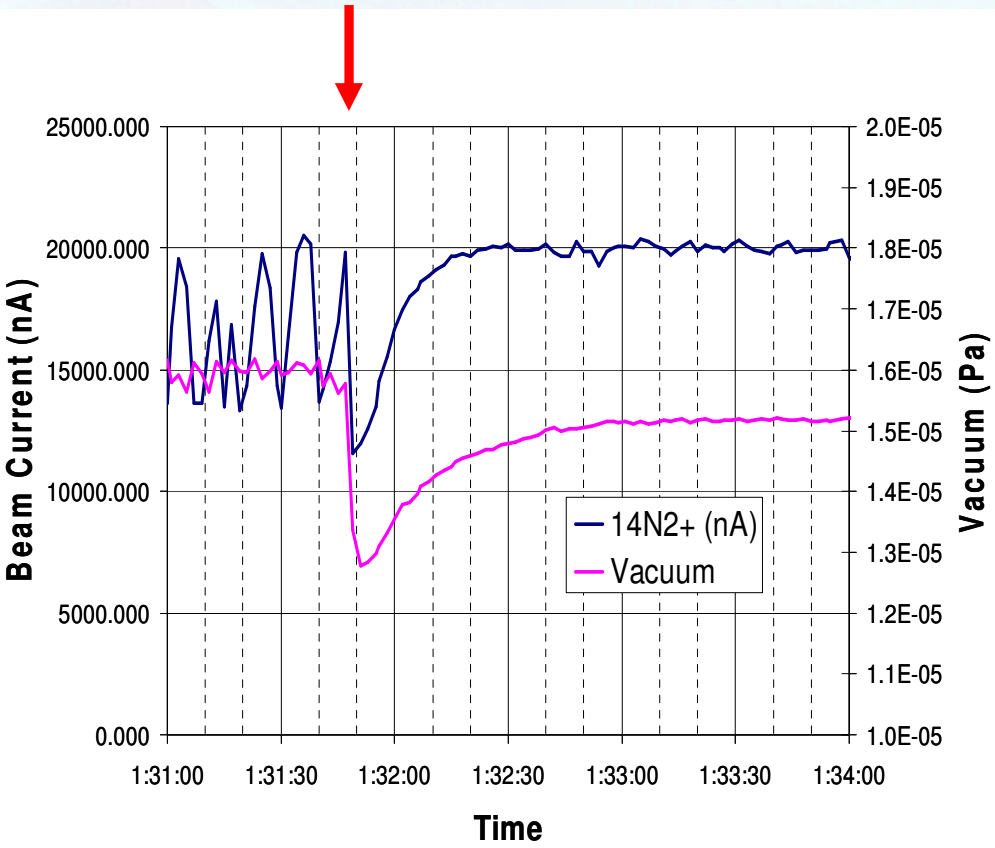
Cross sectional view of the current configuration of the ANSTO ECRIS which allows independent rotation of the hexapole magnetic array, sweeping the electron loss regions across the entire quartz plasma chamber.

ECR ion source issues:

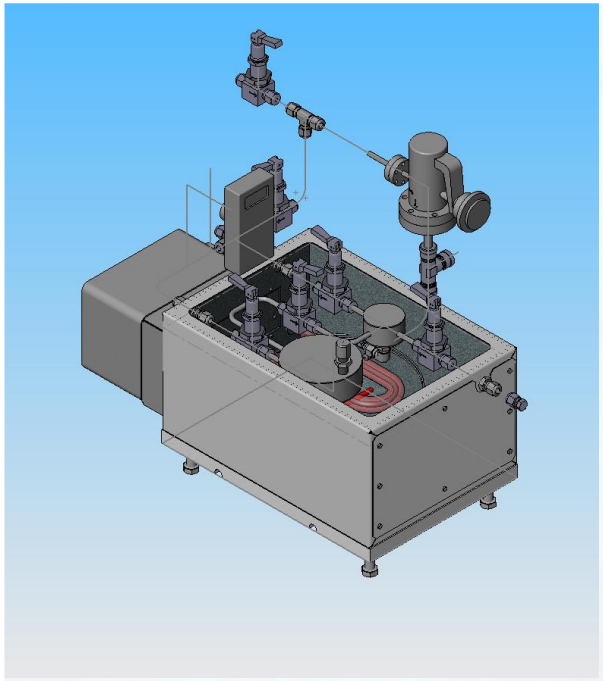
- effect of rotation

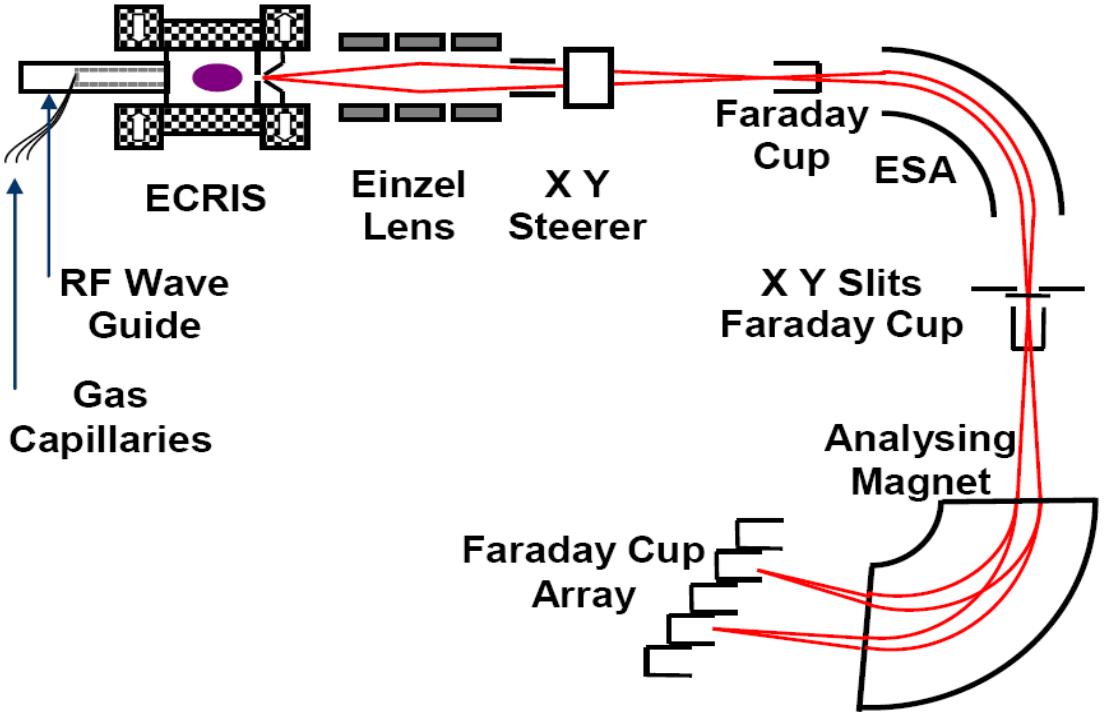


10min injection of N_2 ; after 45 minutes the hexapole rotation was started



Running $^{14}N^{2+}$ beam with the hexapole rotating, then the rotation was stopped.





IRMS++ new configuration:

- inject samples as gas or vapour with carrier or support gas (helium or hydrogen)
- heated injection line for water vapour (see above)
- electrostatic analyser added – eliminate backgrounds from molecular break-up and charge-changing reactions
- multi-collector with 5 Faraday cups

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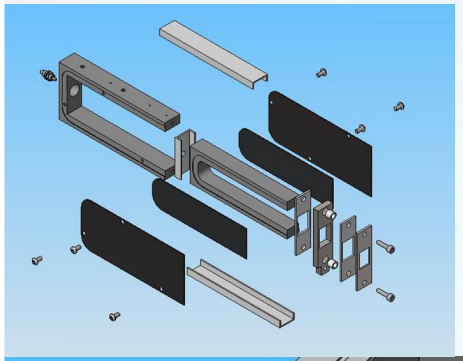
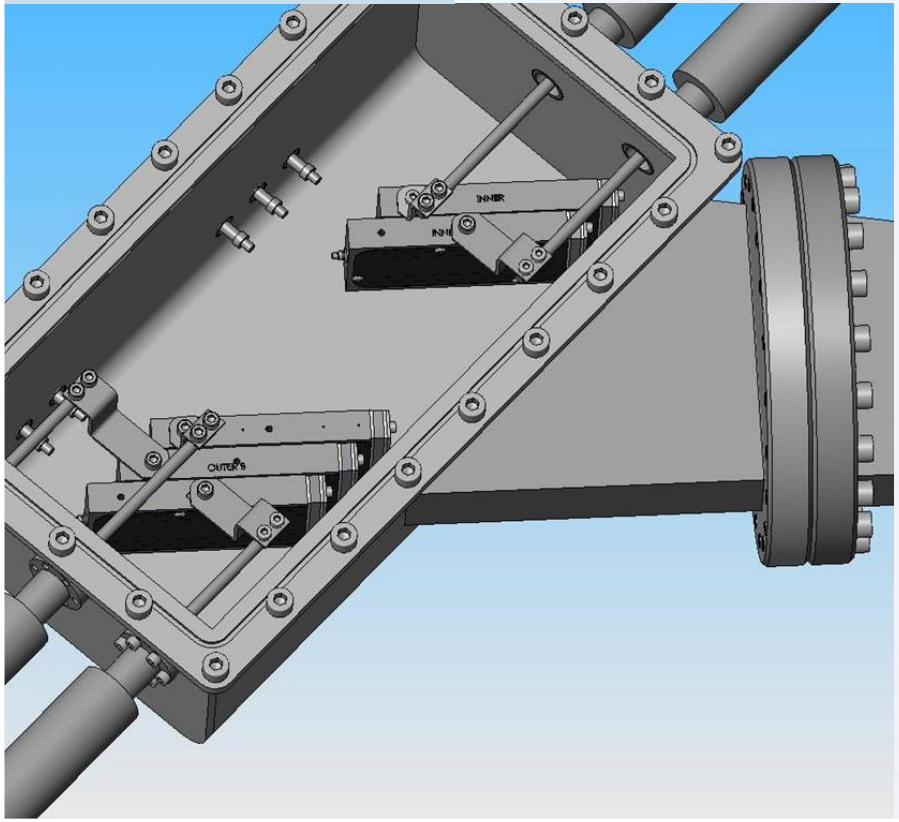
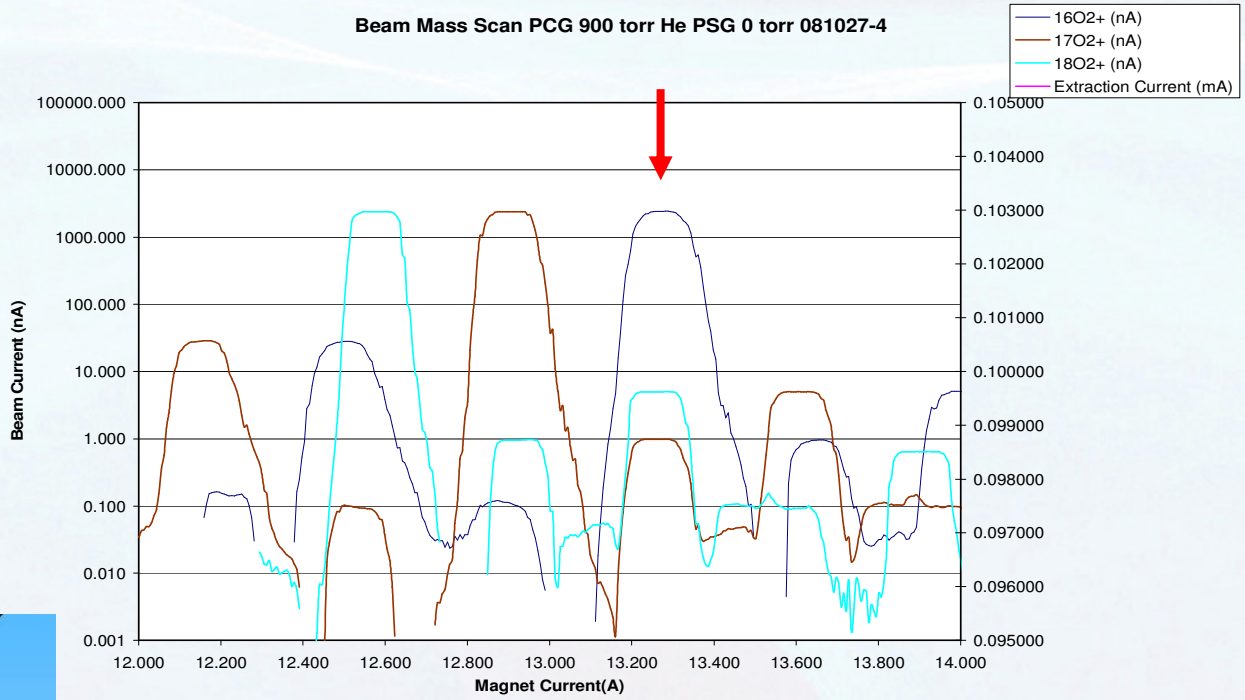
Scans across 3 cups (O2+)







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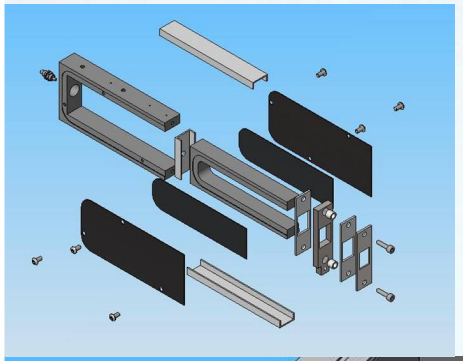
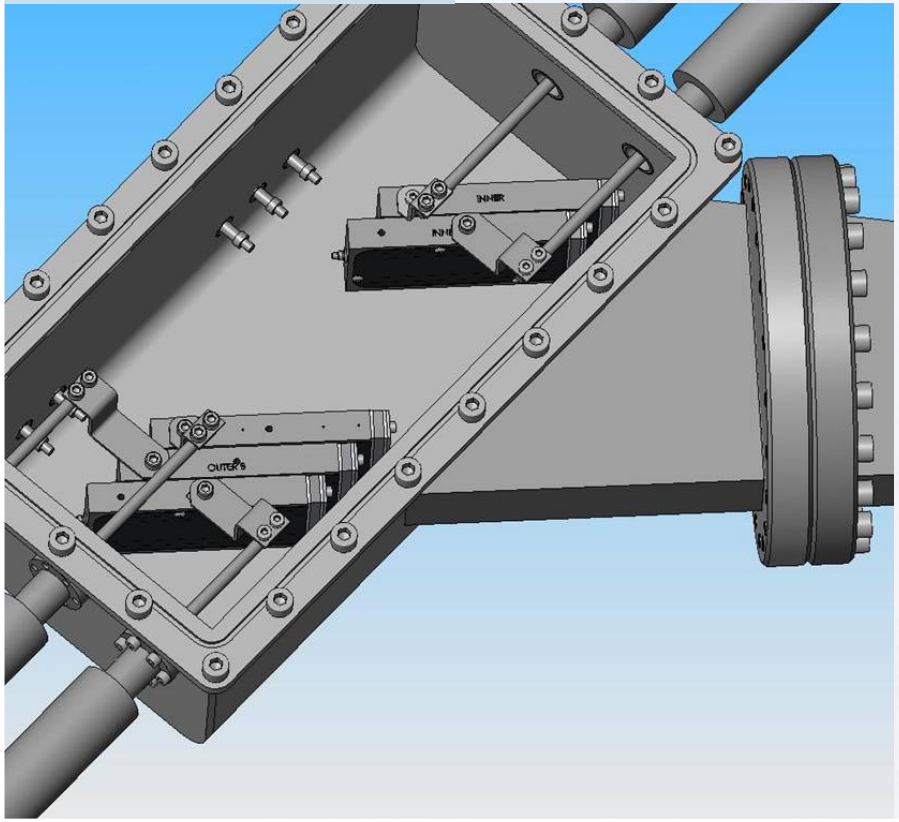
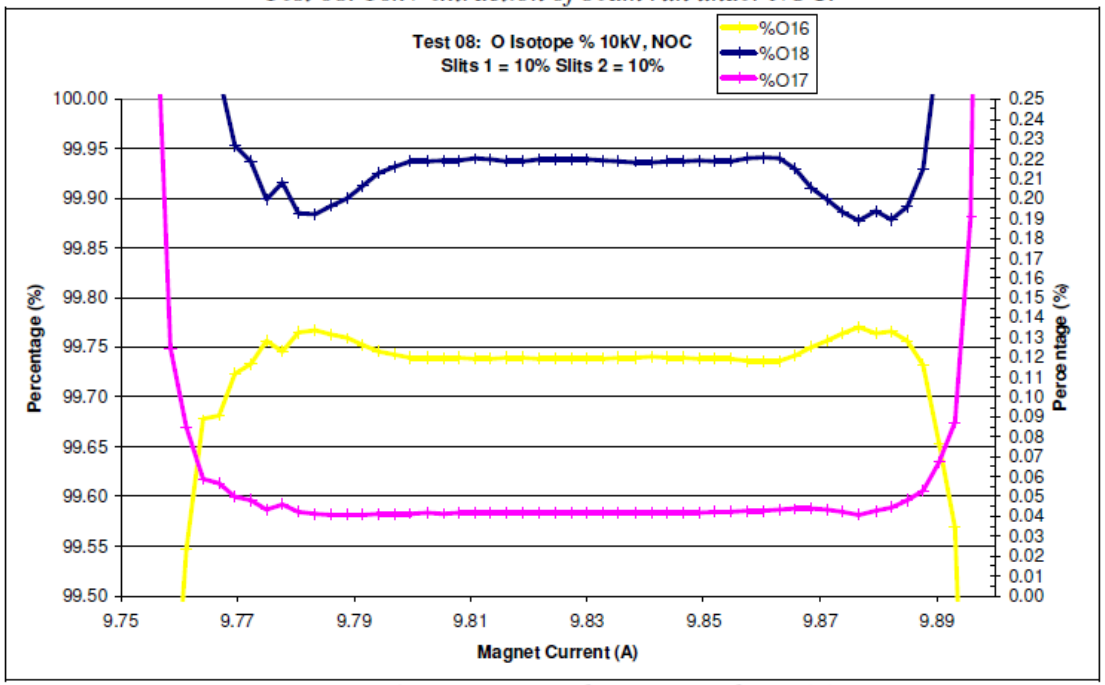
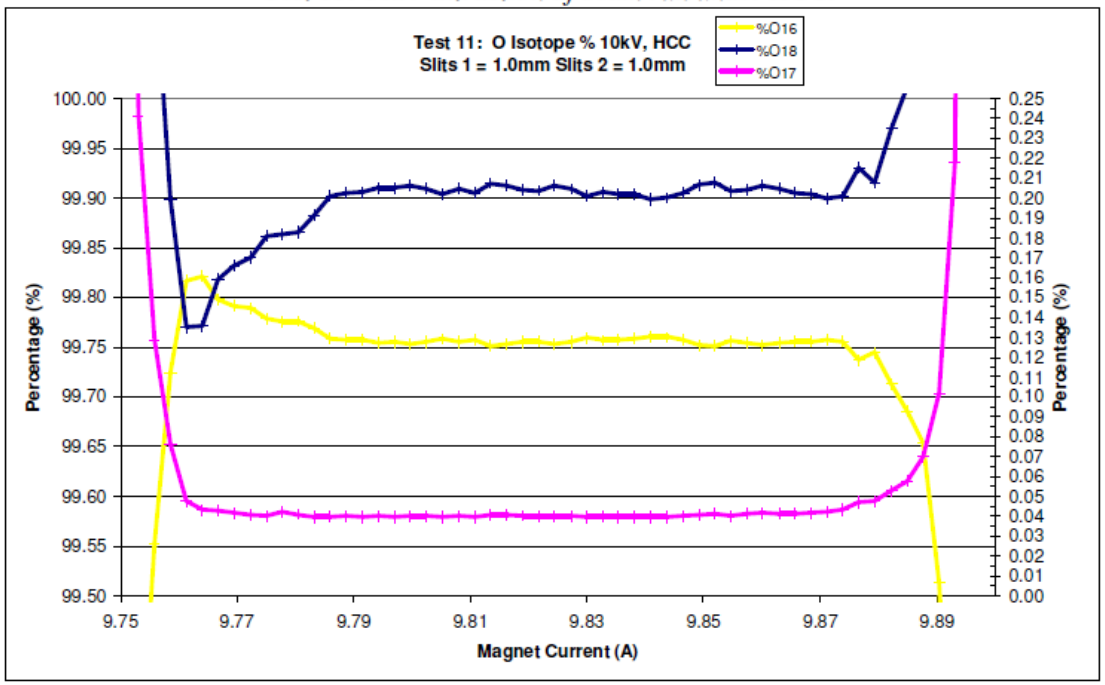




Test 08: 10kV extraction of beam run under NOC:



Test 11: 10kV extraction of beam run under HCC:



ECR ion source issues – solutions

Backgrounds / contamination can be controlled through:

- careful choice of materials
- pre-assembly cleaning procedures
- plasma cleaning, eg oxygen or water plasma to remove carbon; hydrogen plasma to remove water or oxygen

Retention problems:

- minimise plasma chamber volume to ensure effective plasma cleaning
- rotate hexapole (or chamber?)

Conclusions / future developments:

ECR ion source has some interesting possibilities for isotopic mass spectrometry, and its own problems

IRMS++: need for high precision isotopic ratios

- need to resolve problems with water samples

ICE-MS: charge exchange process – needs to be optimised

- improve charge exchange cell
- improved radiocarbon sensitivity with extra analysers

Acknowledgments:

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Thank you!