OPTIMISATION OF A PORTABLE QMS FOR ENVIRONMENTAL MONITORING

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TRACKING ENVIRONMENTAL CHANGE

- Global need for environmental data
- Methods of capturing environmental information *in situ* are few, and limited
- Field analysis restricted by technique
- High reliance on laboratory for complex analysis
- Geographic spread of datasets restricted by technology (cost and portability)

TRACKING ENVIRONMENTAL CHANGE

- Stable isotope measurements (IRMS) inform global trends
- e.g. δ^{13}C falls with increasing CO_2
- Small fluctuations significant
- $\delta(‰) = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000$
- High measurement precision required: better transmission → greater precision
- Other applications: archaeology < 2 (‰) paleobiology, volcanology, geochronology…

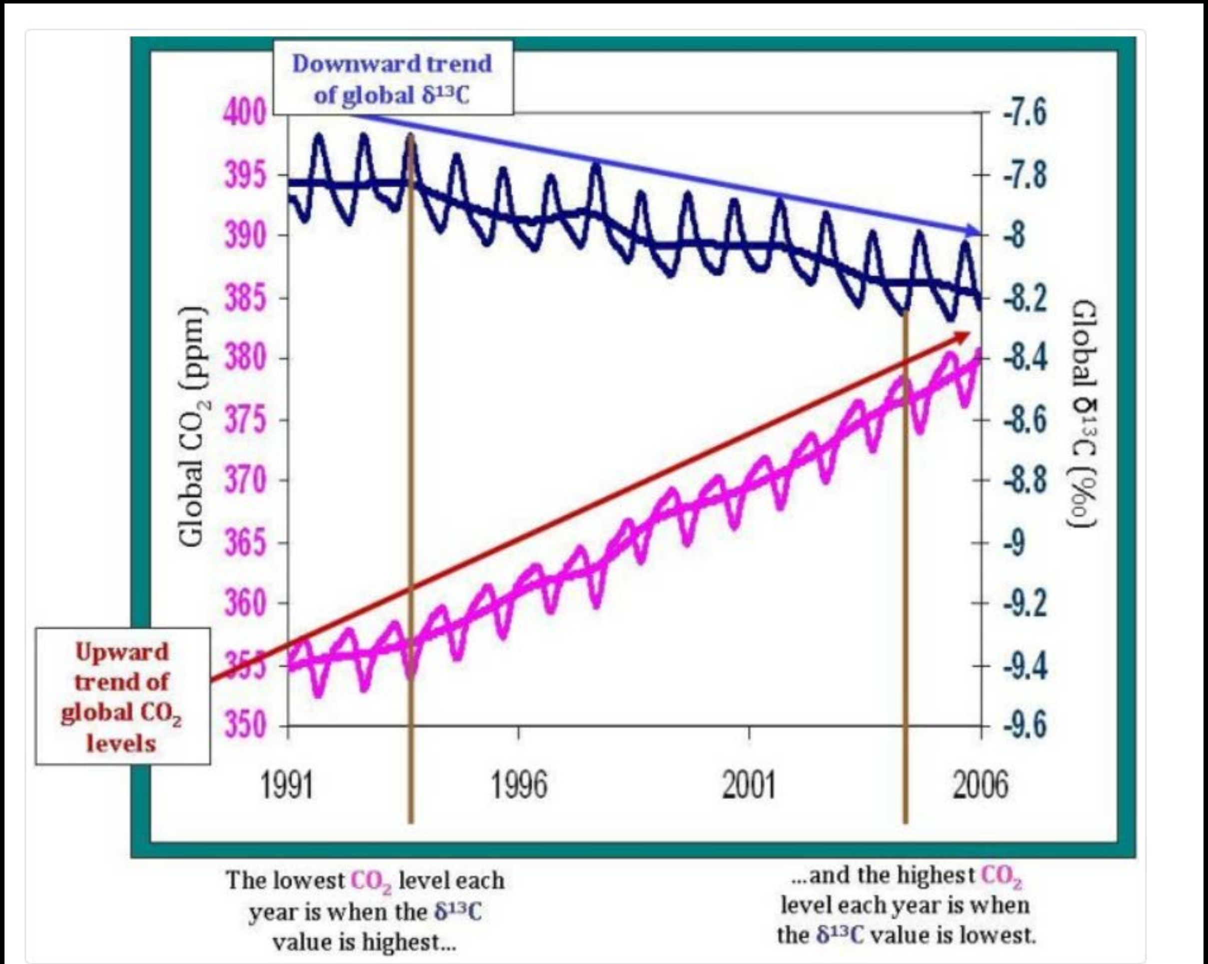


Figure: Earth System Research Laboratory Global Monitoring Division
https://www.esrl.noaa.gov/gmd/outreach/isotopes/c13tellsus.html

THE NEED FOR PERFORMANCE

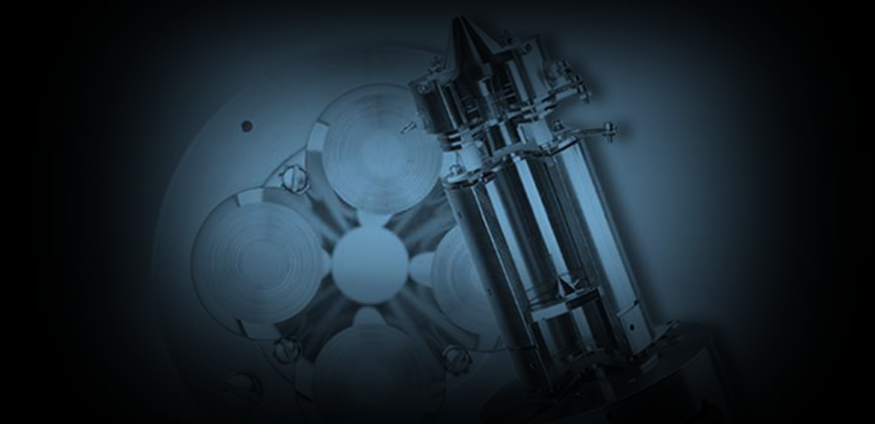
Mass Spectrometry

- **FT-ICR**
- **MALDI-TOF**
- **Orbitrap**
- **AMS**

THE NEED FOR COMPACT

Quadrupole Mass Spectrometry

- **Versatile, scalable and accessible**
- **Simple design and affordable**
- **BUT Smaller → worse performance (usually)**

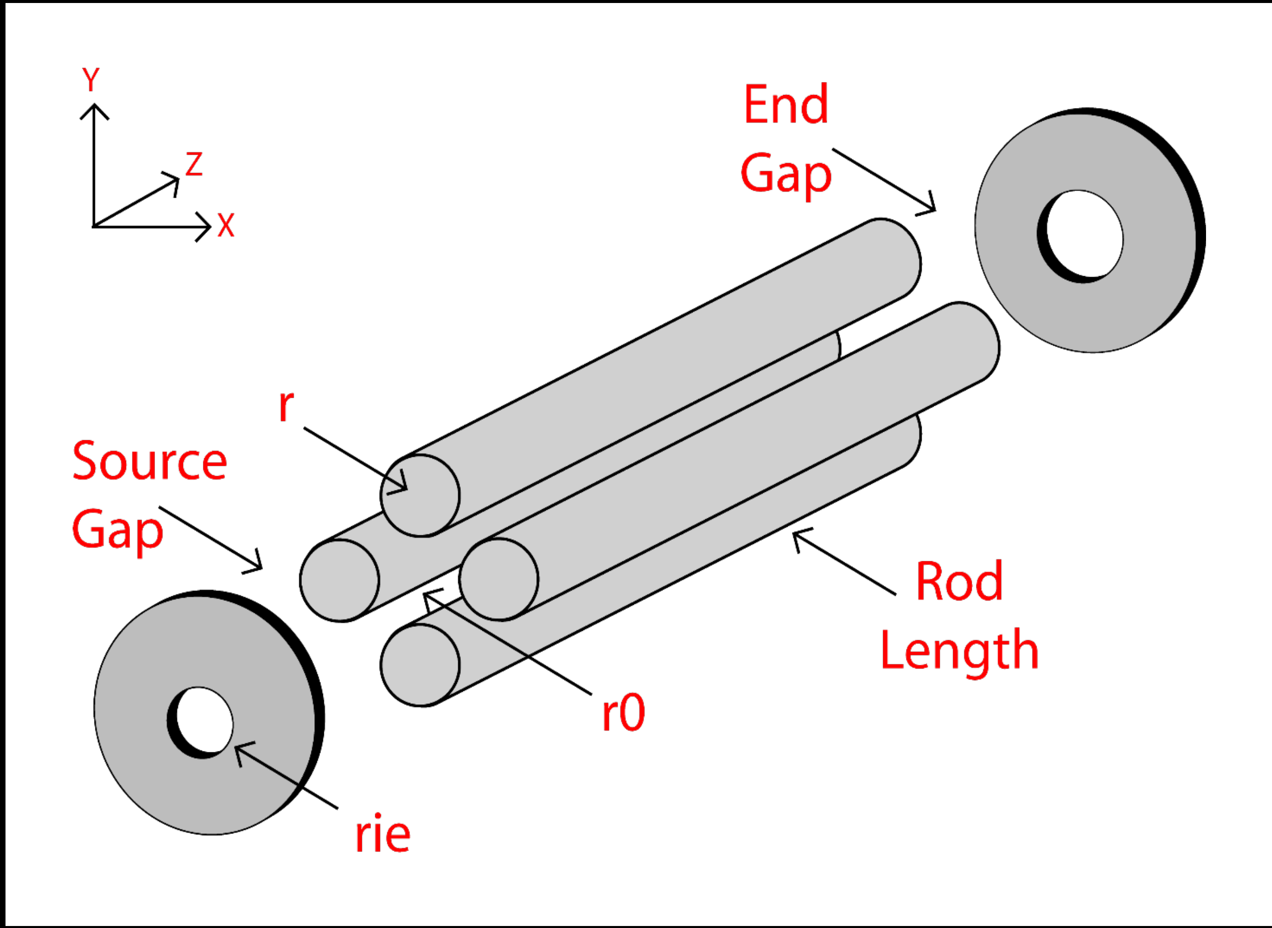


- **Can we improve small footprint QMS performance to allow on-site IRMS?**

QMS OPTIMISATION

Variables…

- Filter geometry
  - Rod length
  - r0
  - r/r0
  - Source gap
  - rie
- Pre/post-filter(s)
- DC offset
- Rod bias



Goals…

- Efficient **transmission**
- Optimal **stability** (precision)

whilst maintaining

- Acceptable **resolution**
- Compact design
- Affordability

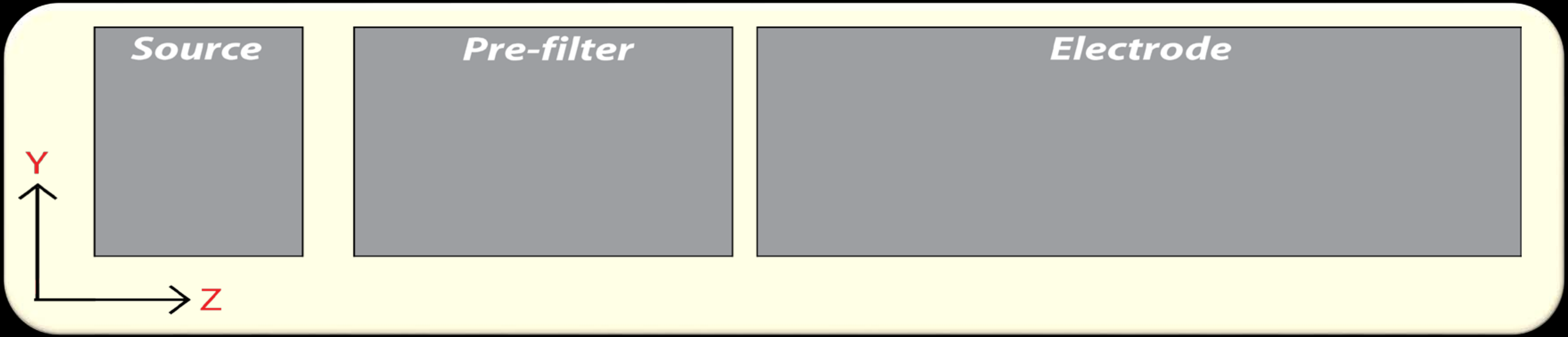
METHODS

Simulations in x, y, z and time supported by experimental measurements

Source Gap *– space between source and QMF (or pre-filter)*

Pre-filter *– RF-only to aid transmission efficiency /stability*

Rod Bias *– DC voltage applied to QMF (and/or pre-filter) electrodes is raised to slow down ions from the source*



SIMULATION TOOL QMS-3D: Stable ion trajectories 3D animation demo

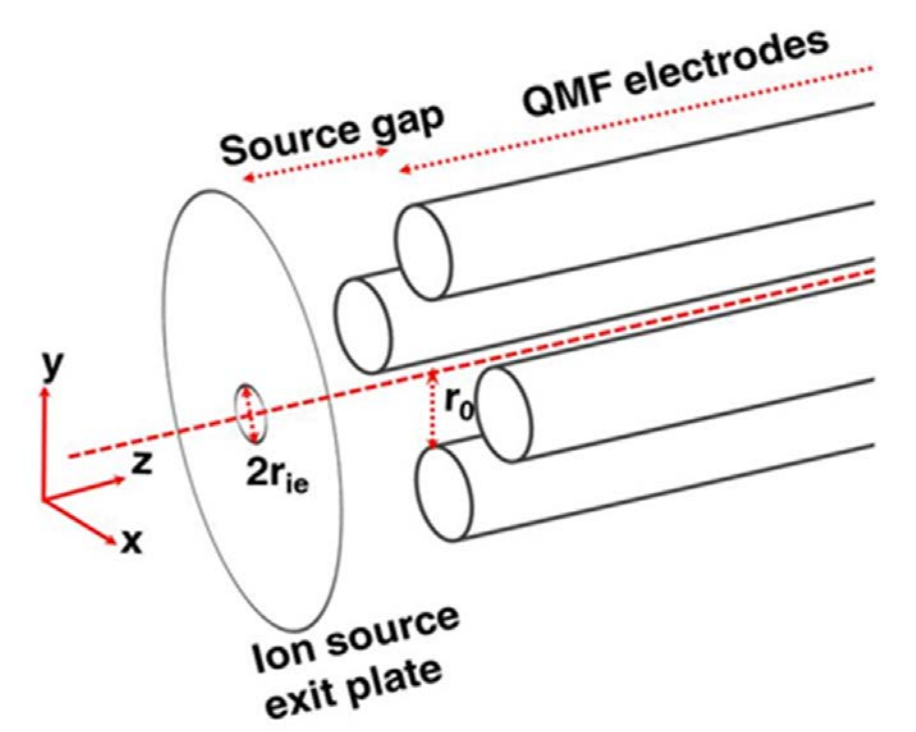
Screen capture from ‘QMS_Traj’ ***(written in MATLAB: D. McIntosh, Mass Spectrometry Group, UoL, UK)***

Unstable trajectory 3D animation demo

Screen capture from ‘QMS_Traj’ ***(written in MATLAB: D. McIntosh, Mass Spectrometry Group, UoL, UK)***

1. SOURCE GAP

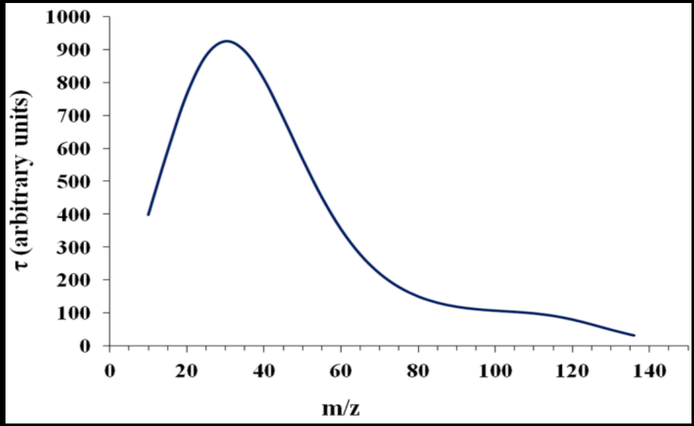
- 3D fringe fields at QMF entrance affect ion transmission: ion motion coupled in x, y and z
- Prior experimental treatments: fringe fields reduce ion transmission efficiency for heavier ions [1,2]
- Heavier ions spend a longer period exposed to defocusing forces in the *y* direction [1,2]

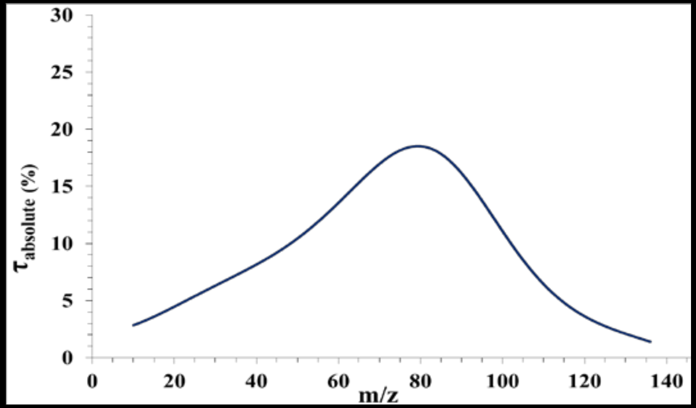


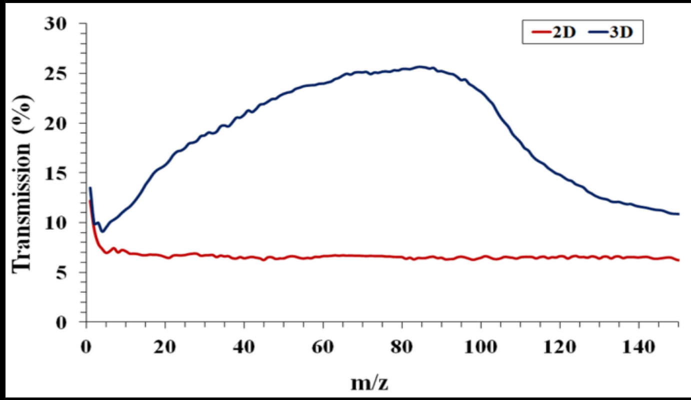
1. Brubaker WM. Auxiliary electrodes for quadrupole mass filters. US Patent 3129327. 14 Apr. 1964
2. Brubaker WM. An improved quadrupole mass analyzer. *Adv. Mass Spectrom* 1968; 4293-299.

2. SOURCE GAP

- Ehlert: isotope ratios → experimental **transmission curve** [1]
- Loss at low m/z … **“artefact”** [1] …..? BUT our experiments (single filter QMS) show both rise and fall are real [2]
- Loss at lower m/z is due to **fringe field effects**
- New method to calculate **absolute experimental transmission**
- QMS-3D simulation model [2, 3] accurately predicts optimum transmission location (in m/z) and percentage



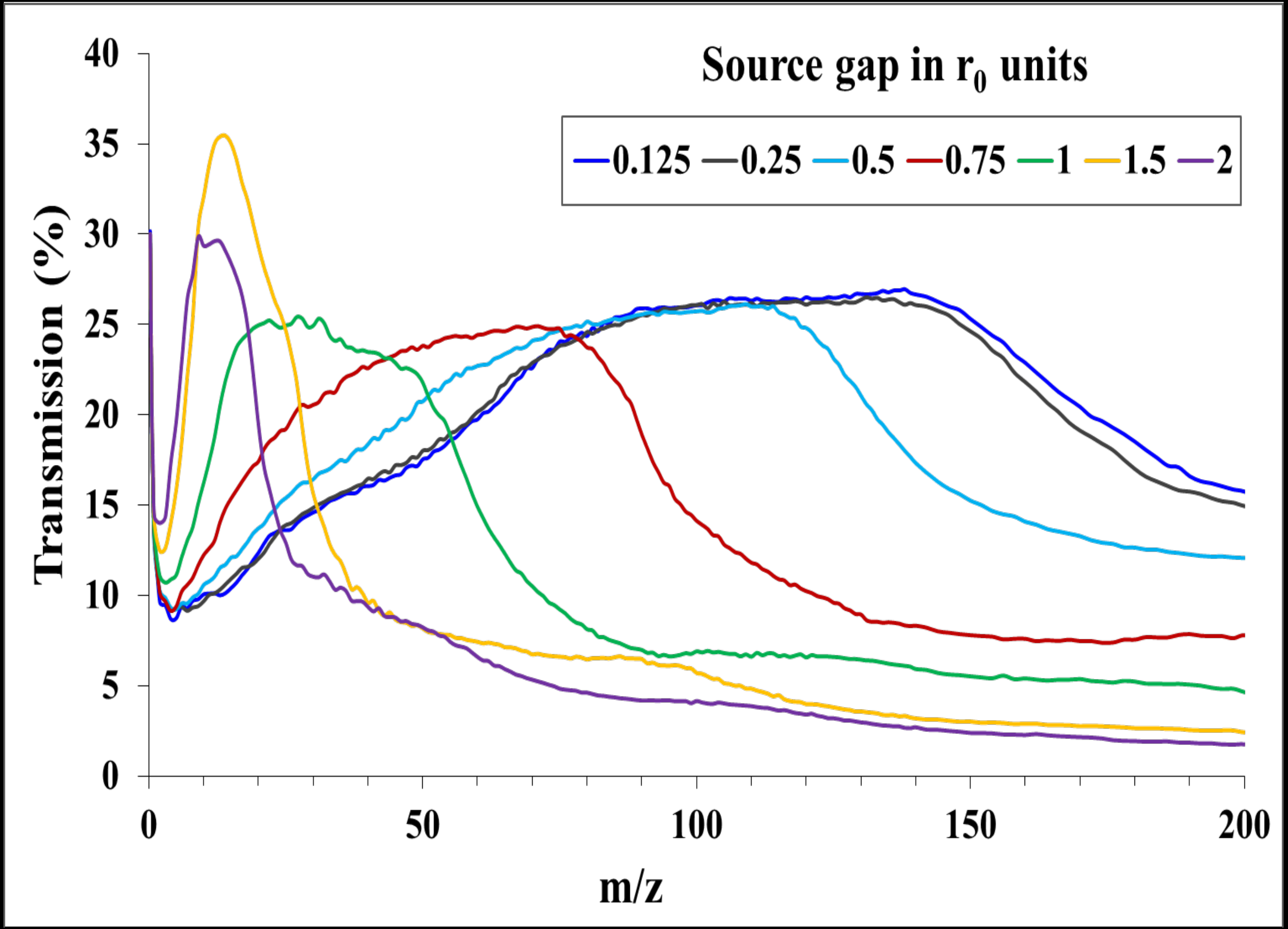




1. Ehlert TC. Determination of transmission characteristics in mass filters. *J.Phys E: Scientific Instr.* 1970; 3(3):237-239.
2. Antony Joseph M, McIntosh D, Gibson R, Taylor S. Effects of the source gap on transmission efficiency of a quadrupole mass spectrometer. *RCMS*, 2018.
3. Gibson JR, Evans KG, Syed SU, Maher S, Taylor S. A method of computing accurate 3D fields of a quadrupole mass filter and their use for prediction of filter behavior. *J.American Society for Mass Spectrometry* 2012; 23(9):1593-1601.

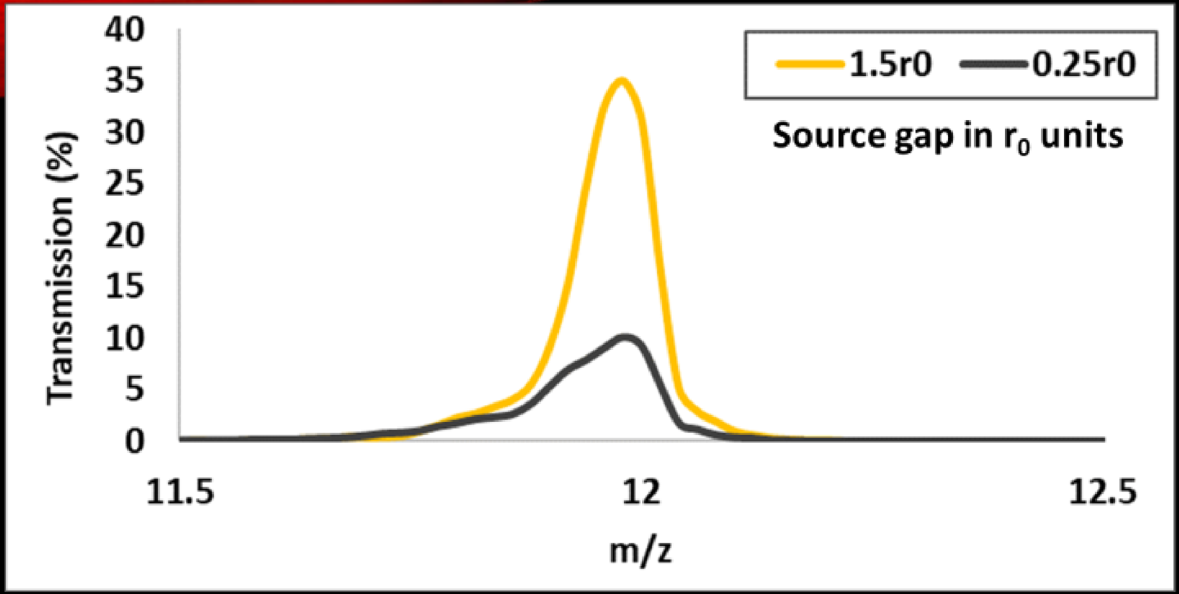
2. SOURCE GAP

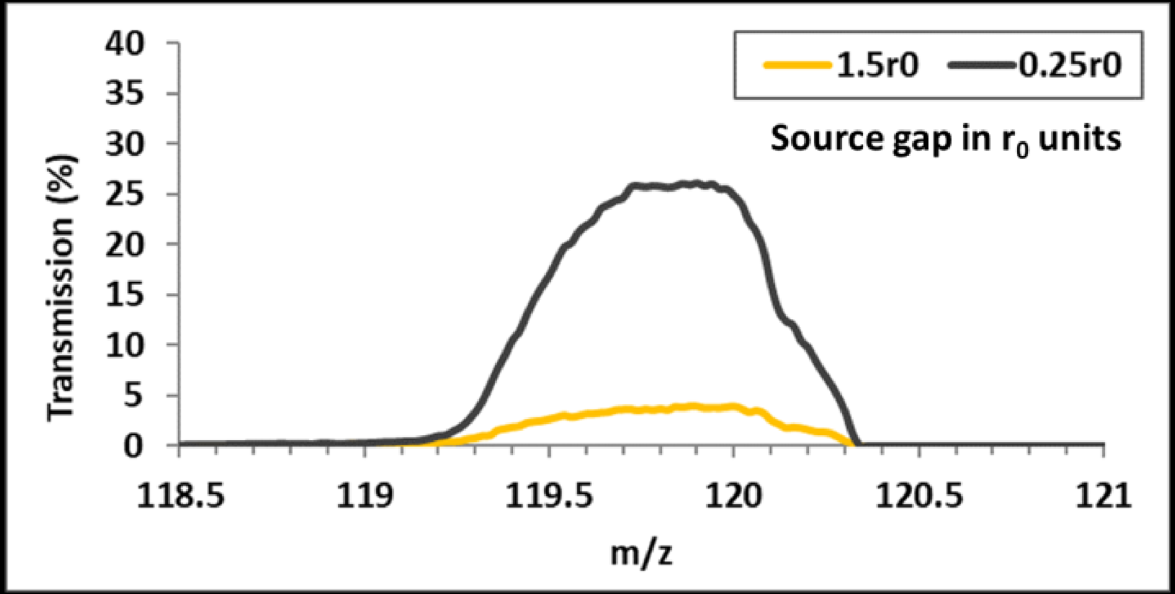
- Length of source gap dictates fringe field length and field intensity
- Not analogous to altering ion energy
- QMS-3D model allows direct study of relationship between physical source gap length and stable ion transmission efficiency
- Different source gap lengths promote peak transmission in different m/z ranges [1]
- **Source gap can be tailored for optimum transmission in desired mass range**



1. Antony Joseph M, McIntosh D, Gibson R, Taylor S. Effects of the source gap on transmission efficiency of a quadrupole mass spectrometer. *Rapid Communications in Mass Spectrometry* 2018.

2. SOURCE GAP

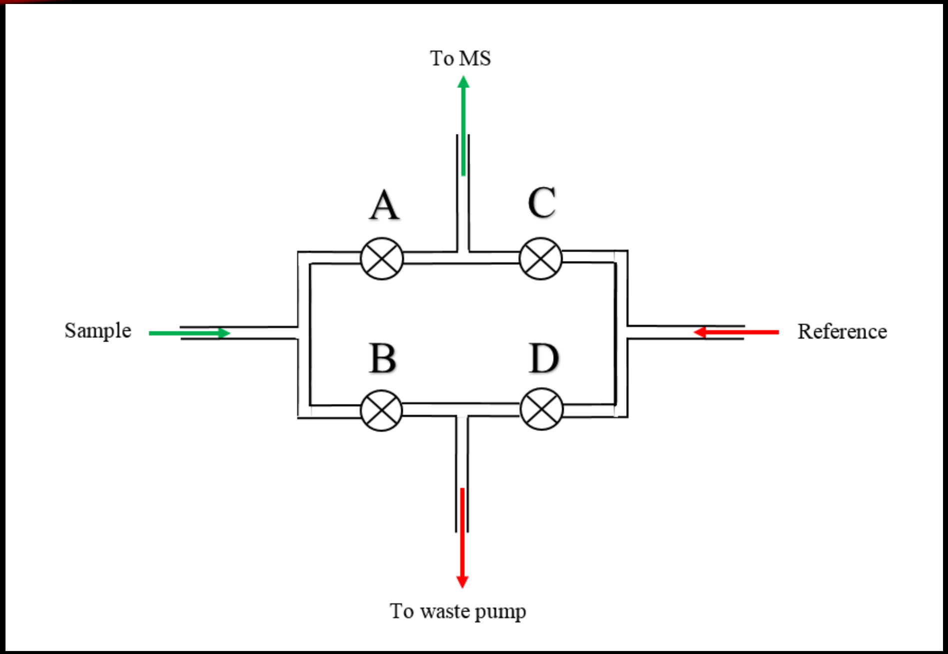




- Smaller source gaps → optimal transmission at higher m/z and vice versa [1]
- E.g 1.5r0 source gap improves transmission at m/z 12, but for m/z 120, 0.25 r0 source gap is better
- Transmission gains are not at the expense of resolution
- Source gap optimisation: a critical component of QMS design for mass-specific applications [2,3]
- Accurate simulation of the specific instrument is key

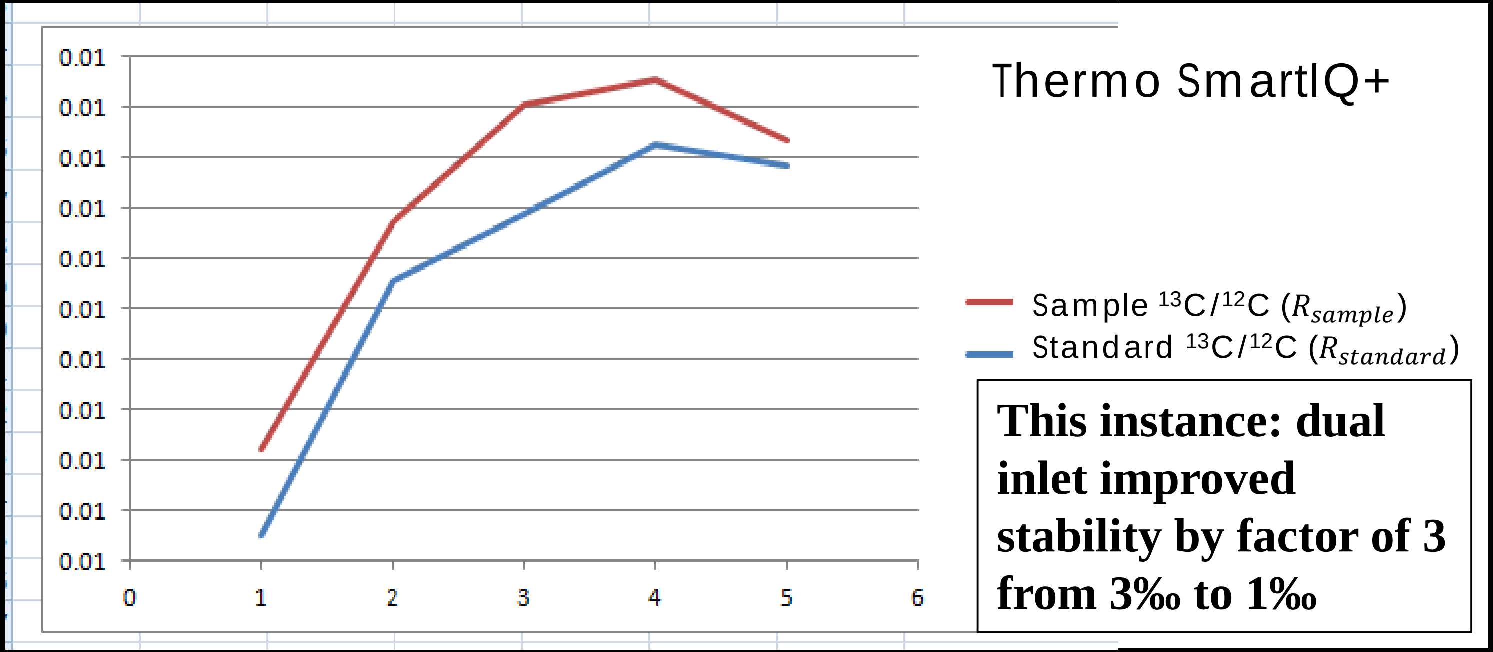
1. Antony Joseph M, McIntosh D, Gibson R, Taylor S. Effects of the source gap on transmission efficiency of a quadrupole mass spectrometer. *RCMS* 2018.
2. Ellefson RE, Moddeman WE, Dylla HF. Hydrogen Isotope Analysis by Quadrupole Mass-Spectrometry. *Journal of Vacuum Science & Technology* 1981; 18(3):1062-1067.
3. Schneider B, Kuiper K, Postma O, Wijbrans J. Ar-40/Ar-39 geochronology using a quadrupole mass spectrometer. *Quaternary Geochronology* 2009; 4(6):508-516.

UPDATE: BRIEF PROGRESS IN $\delta^{13}C$ STABLITY



- Example of progress excluding current optimisation study
- **Dual Inlet:** well established standard stable isotope apparatus
  - Subtraction of temporal instability

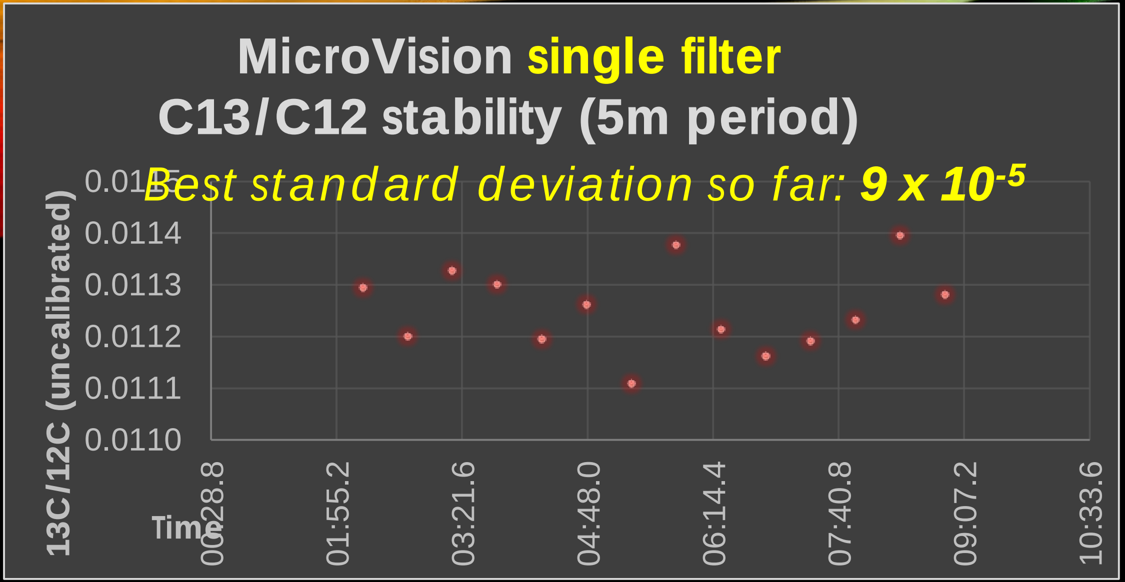
$$\delta(‰) = \left(\frac{R_{sample} - R_{standard}}{R_{standard}}\right) \times 1000$$

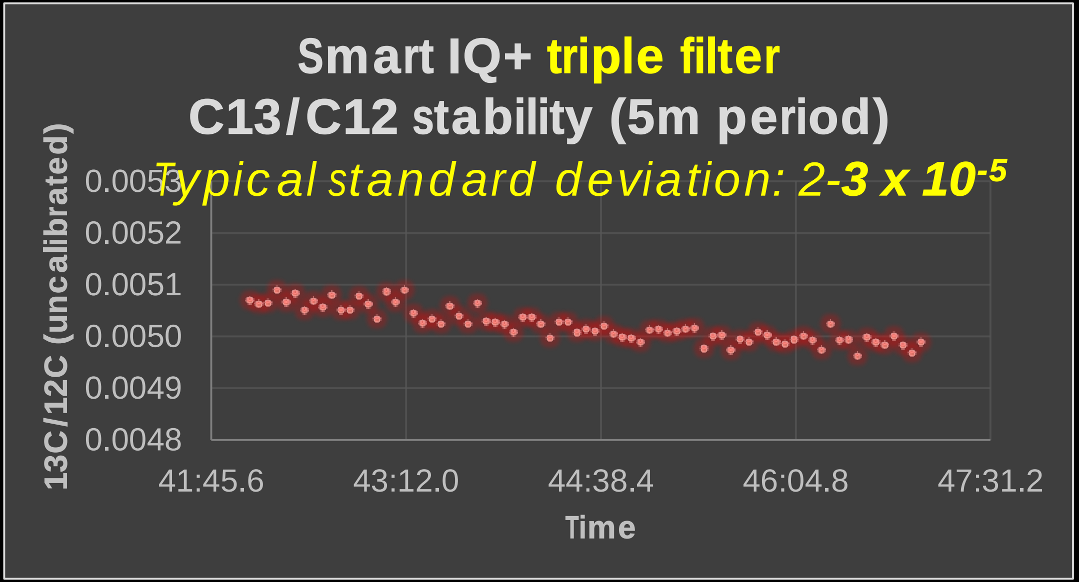


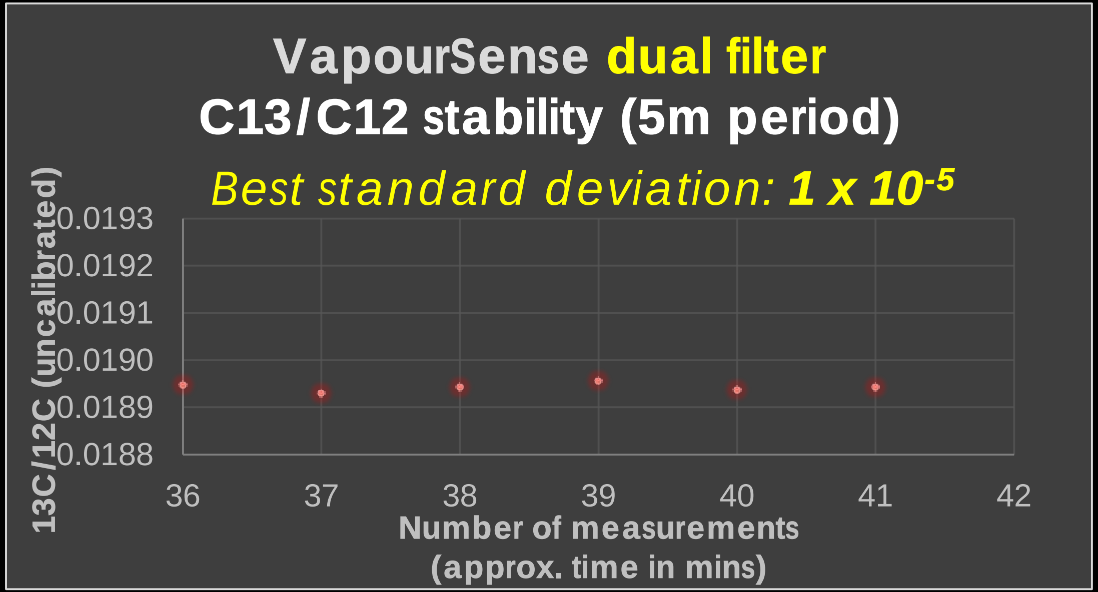
- *Instruments sold / in service*

www.q-technologies.co.uk

PRE-FILTER EFFECT?



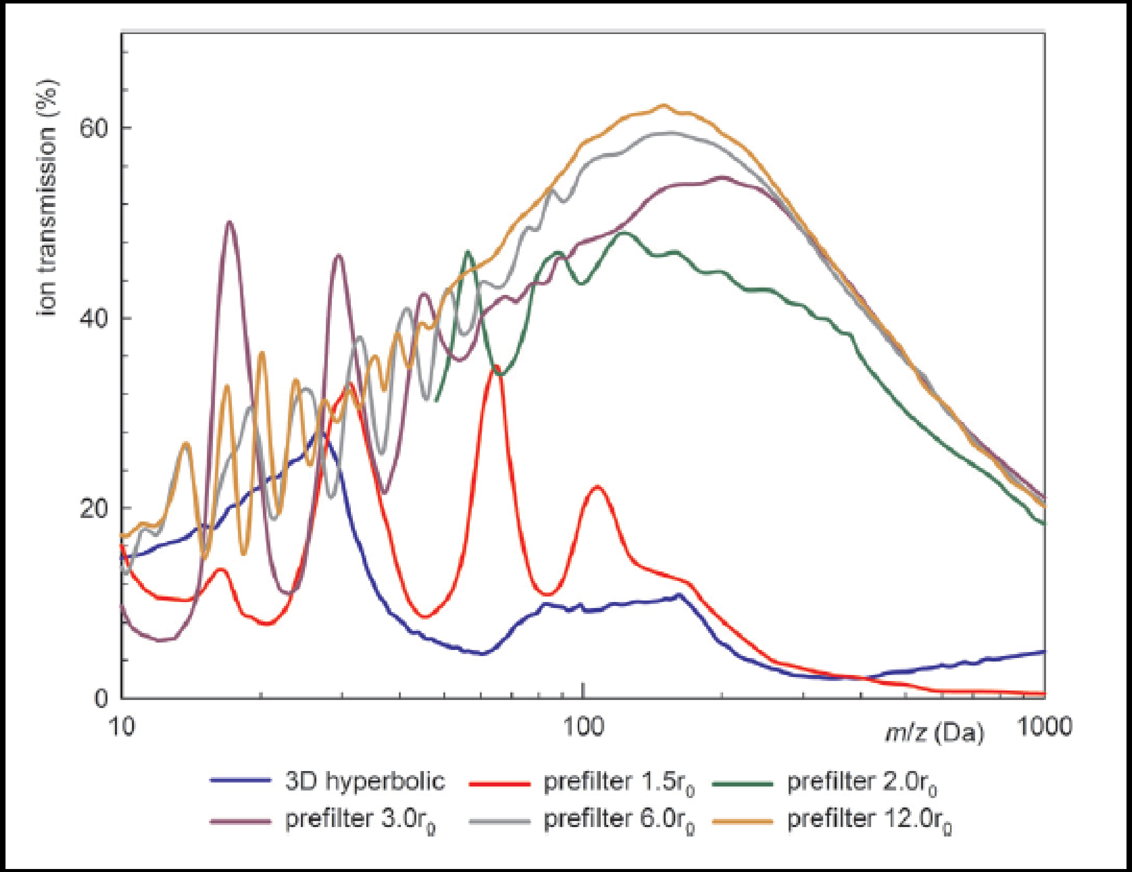




- With crimped capillary inlet, sample CO_2 @ ~34 psi
- Comparison not strictly fair: different geometries modes /settings of acquisition/ on-board signal processing…
- Could pre-filter be a factor? Simulation a fairer test

2. PRE-FILTER

- Brubaker used a delayed D.C. ramp (pre-filter) to reduce the effects of source gap fringe fields [1, 2]
- Improved transmission of low velocity ions (high m/z)
- Using QMS-3D simulation, can design a minimum prefilter length for given electrode, frequency and ion energy [3]
- Caution: for low m/z ions (high velocity), see transmission 'fluctuations' (function of ion velocity)



Ion transmission for several lengths of prefilter

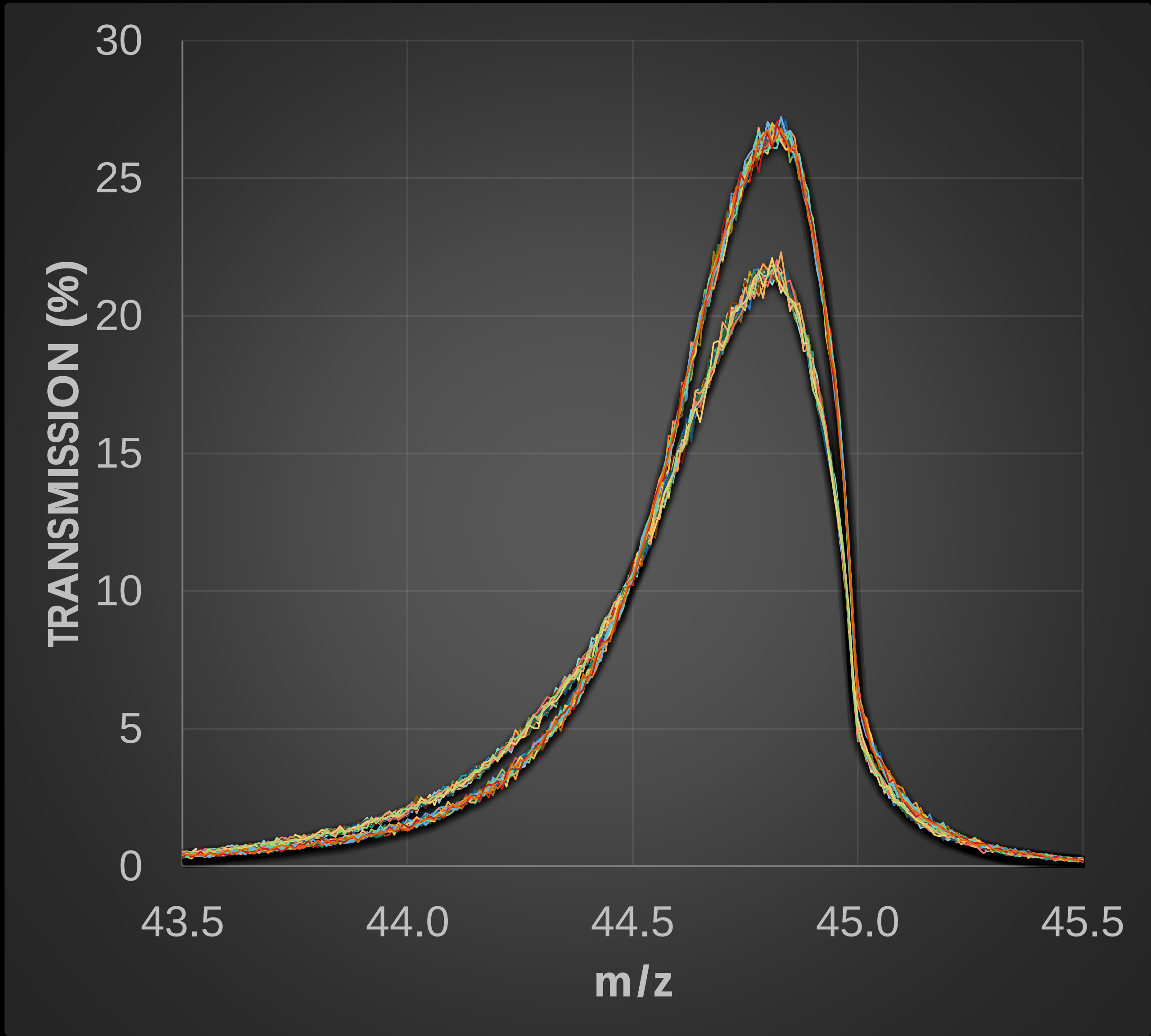
References

1. Brubaker WM. Auxiliary electrodes for quadrupole mass filters. *US Patent* 3129327. 14 Apr. 1964
2. Brubaker WM. An improved quadrupole mass analyzer. *Adv. Mass Spectrom* 1968; 4293-299.
3. Gibson JR, Evans KG, Taylor S. Predicted behaviour of QMF systems with and without prefilters using accurate 3D fields. *Int J.of Mass Spec.* 2017; 422197-207.

QMS-3D Simulations

2. PRE-FILTER

- With and without prefilter
- 20 scans each, 20,000 ions/scan
- Upper series: with prefilter
- Transmission: 23-24% improvement
- *Slight* improvement in resolution (FW @ 10%)
- Effect on quantitative measurement stability?



Simulations: stability predictions

2. PRE-FILTER

	Single filter	Dual filter	Effect
Average Trans.	21.8%	26.9%	23% better
Standard deviation	0.23	0.17	24% better
RSD	**1.03%**	**0.64%**	**38% better**

Tracking maximum transmission

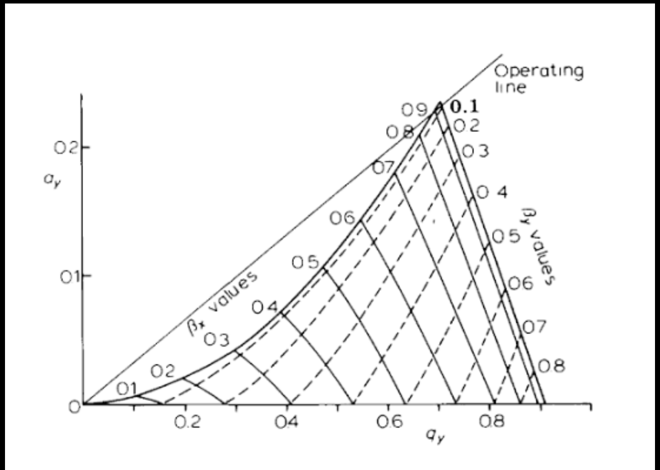
	Single filter	Dual filter	Effect
Average Trans.	21.57%	26.71%	24% better
Standard deviation	0.24	0.26	**9% worse**
RSD	**1.12%**	**0.98%**	**12% better**

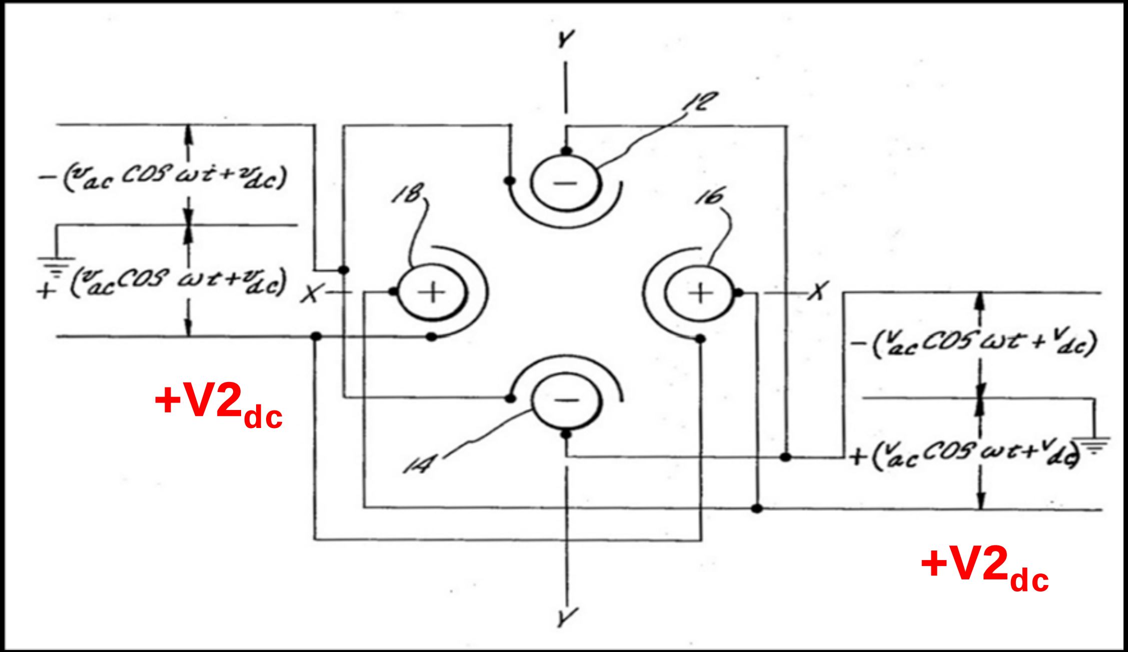
Transmission at a fixed m/z point

- Pre-filter boosts transmission and improves quantitative measurement reproducibility
  - Worse standard deviation in the fixed m/z case could imply an effect on mass filtering accuracy (‘fluctuations’ relevance?? … more study required)

3. ROD BIAS

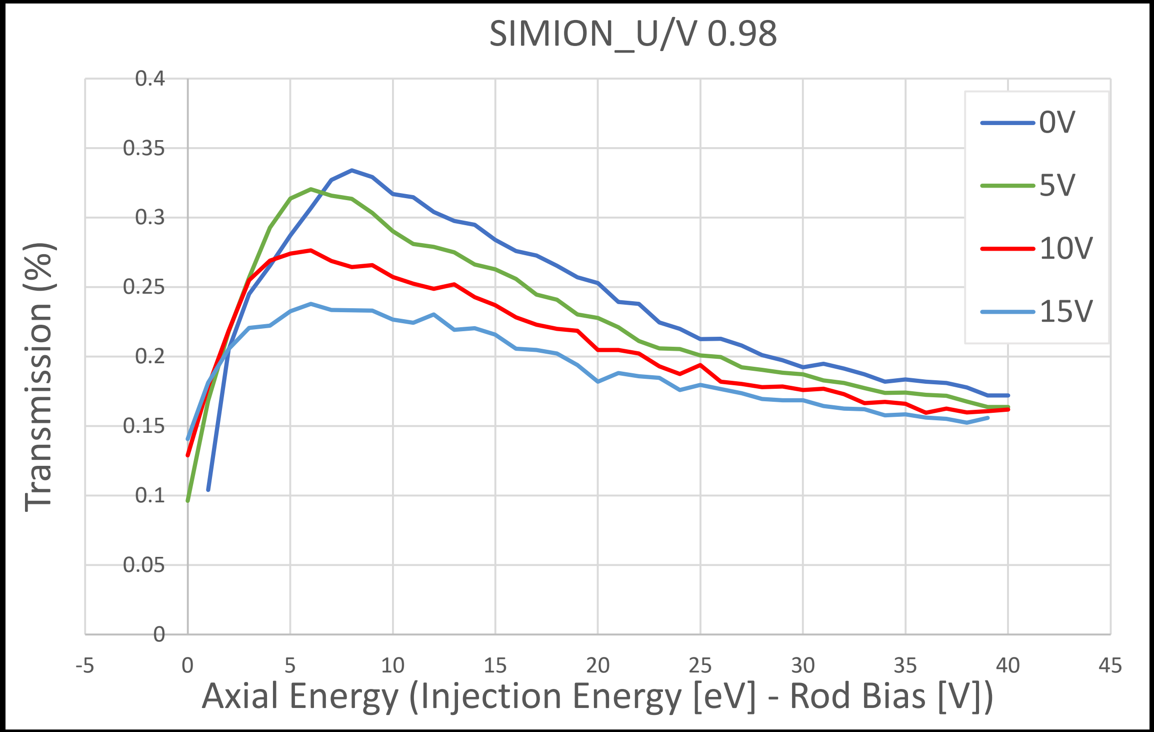
- DC bias of all electrodes in one direction
  - Independent of rod initial mean polarity
- Rod bias alters mean potential gradient in entrance fringe field
- Can be applied:
  - directly to electrodes
  - inversely to entrance / exit plates
- Slower ions → more RF cycles → greater resolution for the same transmission (and vice versa) ?

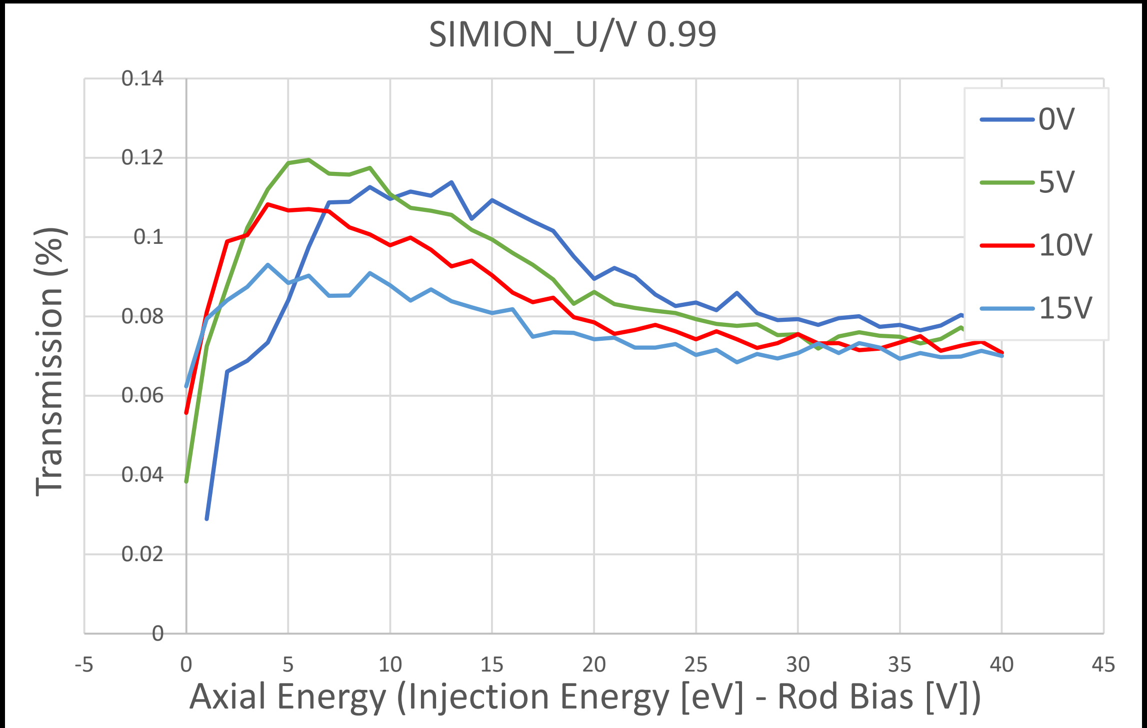




Stability diagram - Dawson, Peter H., ed. *Quadrupole mass spectrometry and its applications*. Elsevier, 2013.
QMF electrical diagram - Brubaker, Wilson M. "Auxiliary electrodes for quadrupole mass filters." U.S. Patent No. 3,129,327. 14 Apr. 1964.

3. ROD BIAS



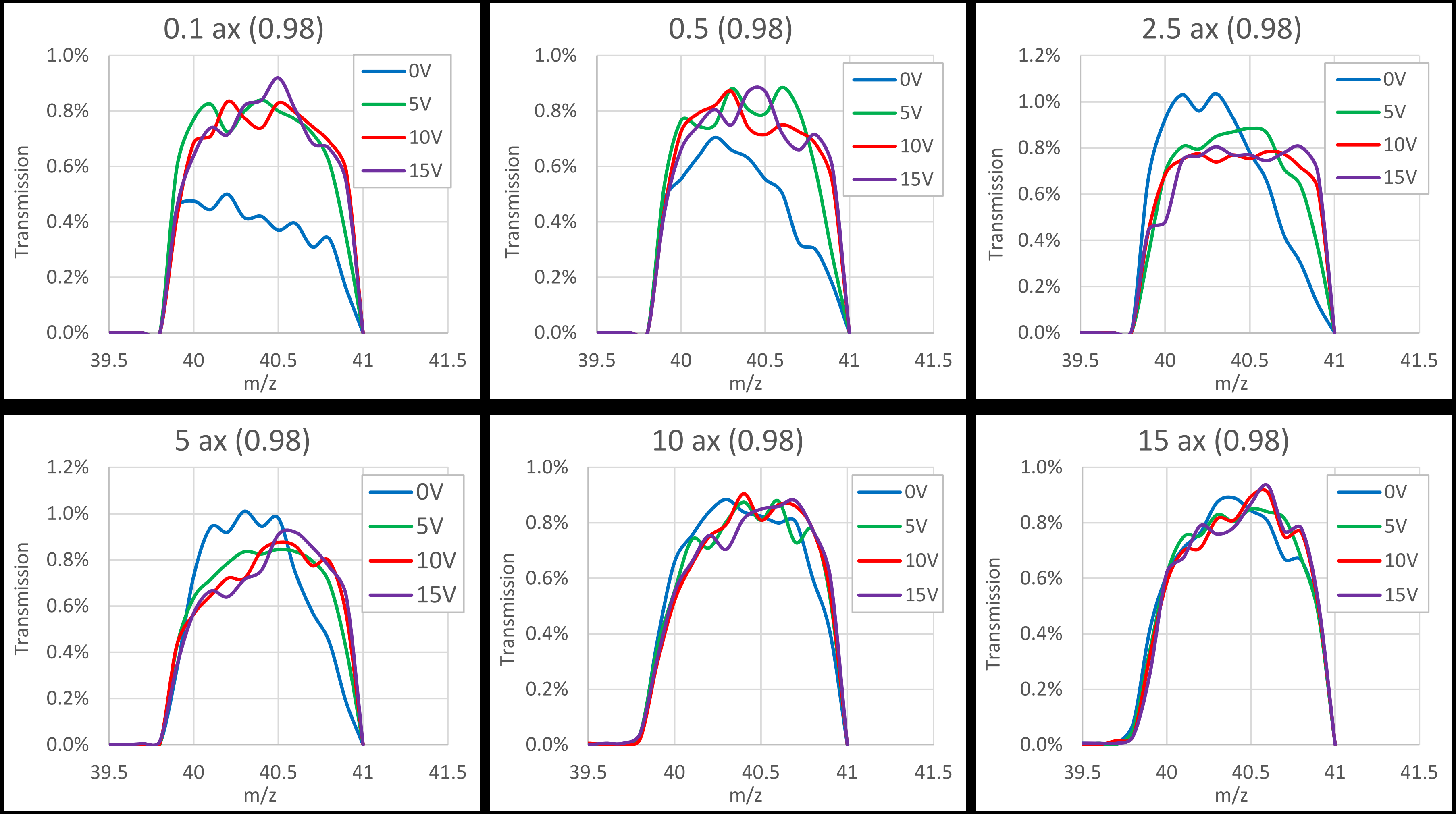


- Use easily variable SIMION ion optics to simulate rod bias effects
- Transmission trend plotted against "Axial Energy (Ae)" for varying rod bias
- At lower Ae, transmission with biased rods surpasses unbiased rods
- Effect is more pronounced at higher resolution (U/V ratios)

Low resolution study

3. ROD BIAS

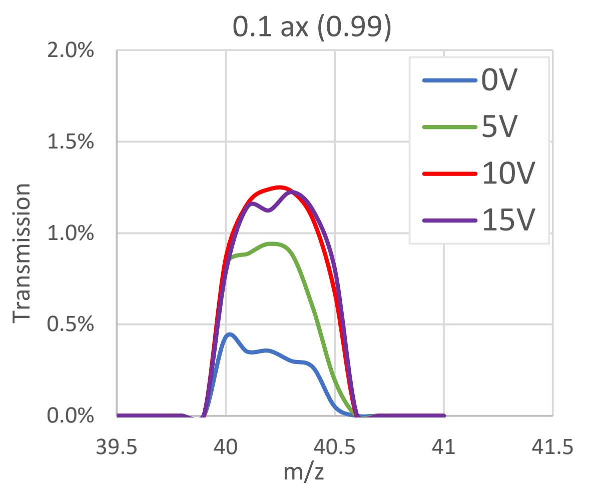
- Rod bias → low axial energies
- Rod bias improves transmission at extremely low axial energies
- Improvement in peak shape with added bias
- Resolution constant

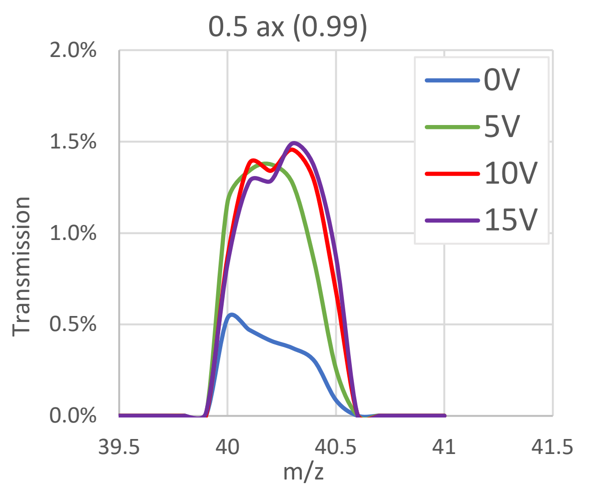


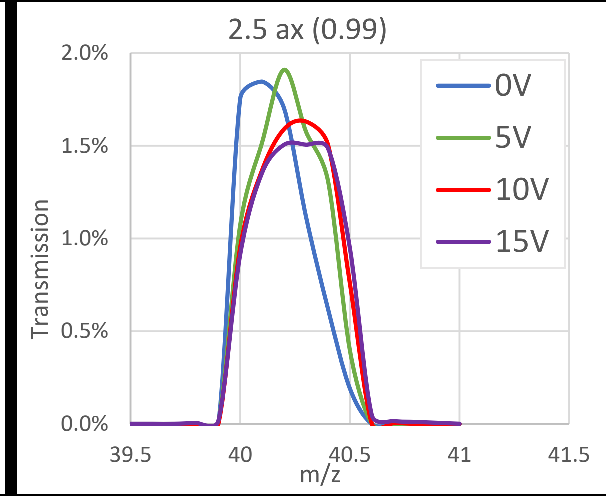
Higher resolution study

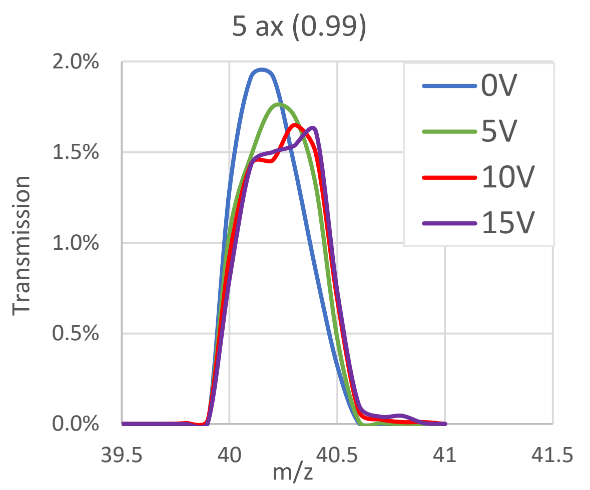
3. ROD BIAS

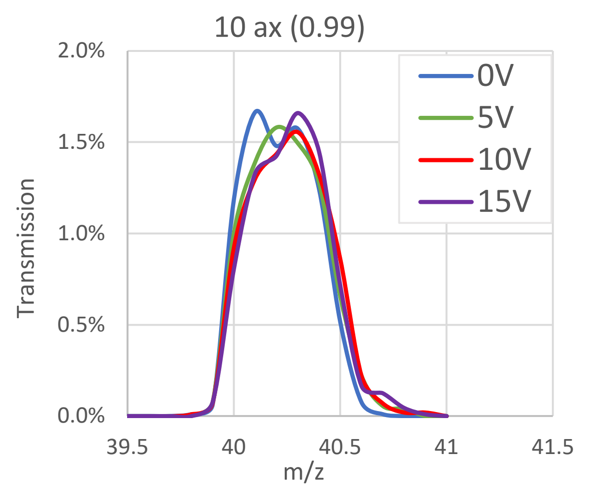
- Rod bias: best at low axial energies
- Allows greater transmission without significantly compromising resolution

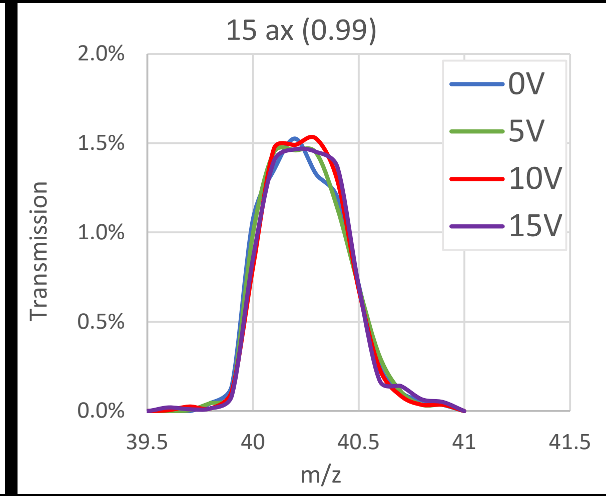








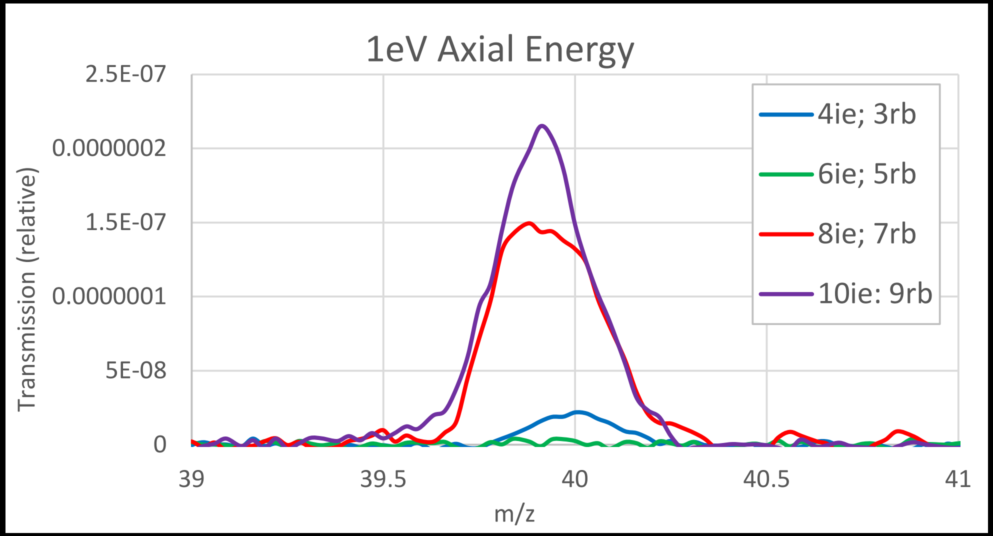


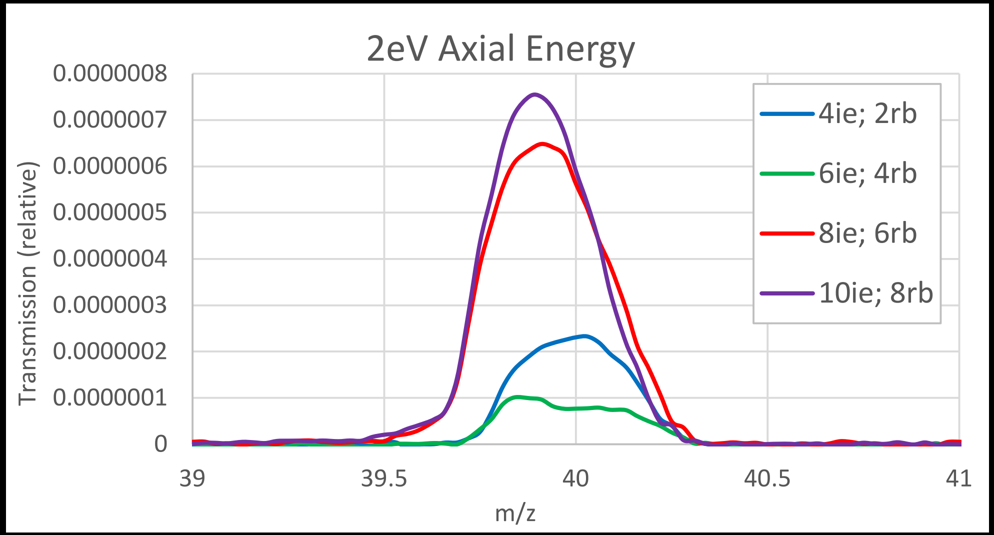


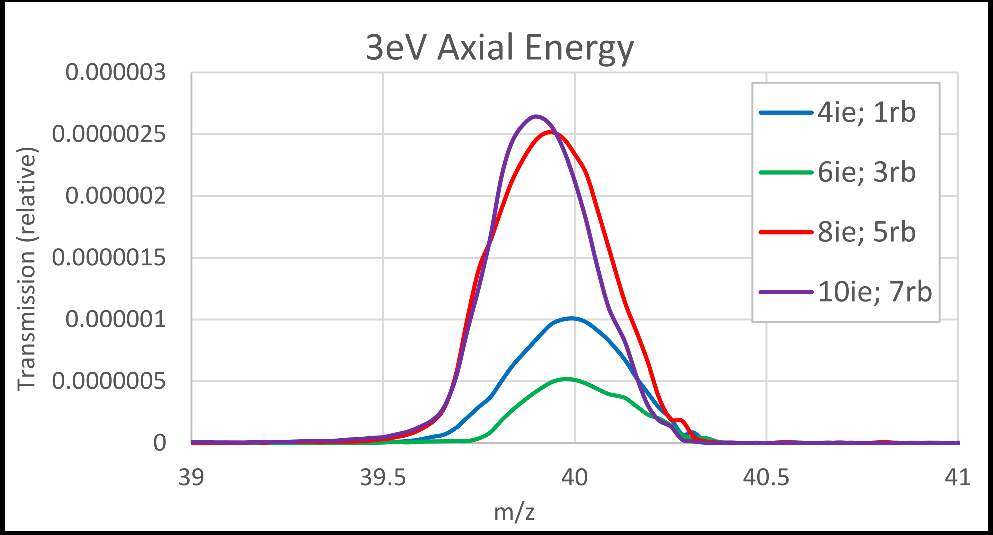
3. ROD BIAS

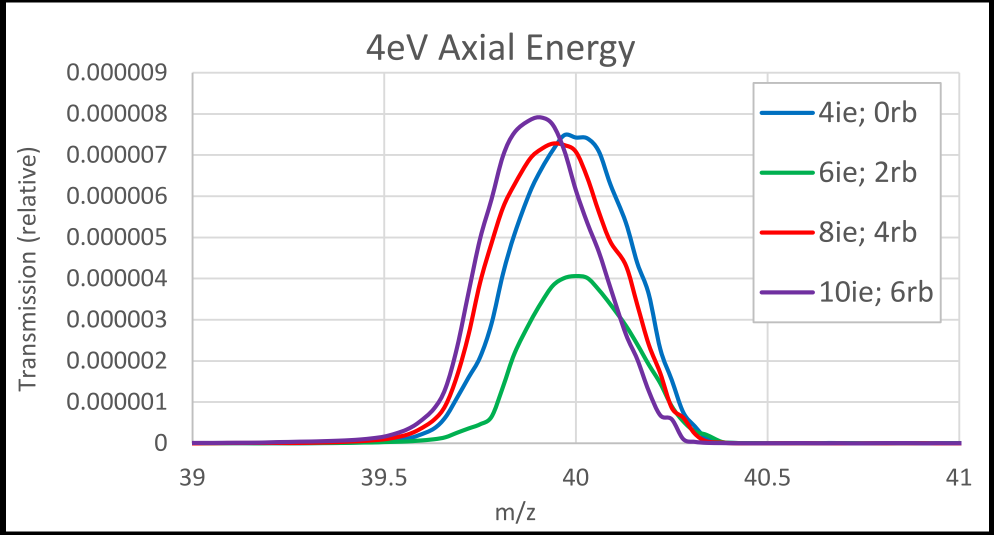
Experimental (single filter QMS)

- Axial energies by varying injection energies (ie) and rod bias values (rb)
- At lower Ae some rb:ie values allow improved transmission without resolution cost



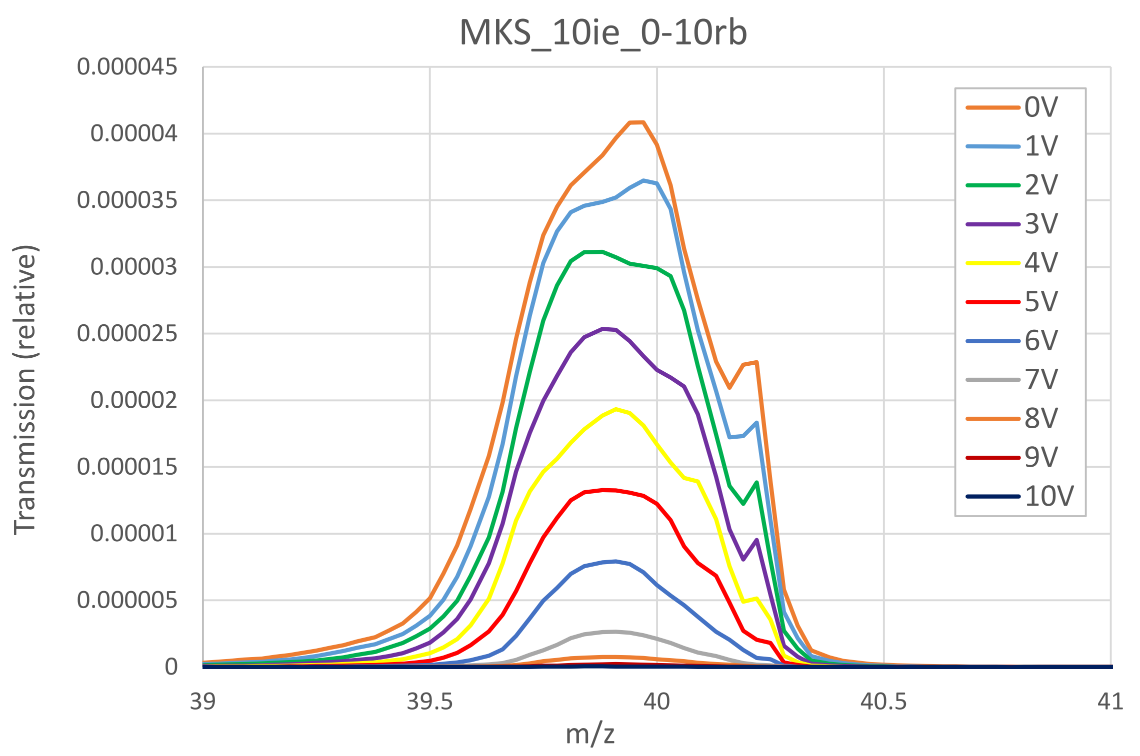


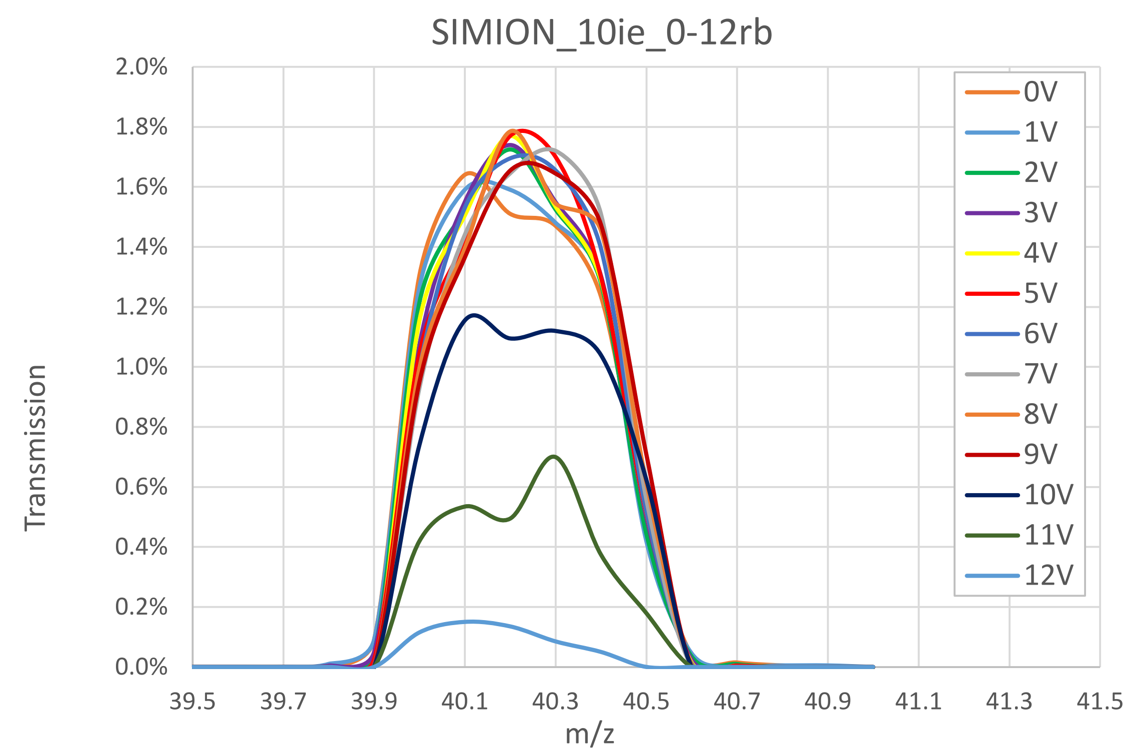




Experimental v SIMION

3. ROD BIAS





- Ion injection energy of 10eV, increasing rod bias from 0-10V
- Experiments: steady incremental drop; simulations: more dramatic decline, as **rb --> ie**
- Different parameters (e.g. source gap)? Unknown factors?

SUMMARY

Isotope Ratio MS (IRMS) needs high ion transmission to achieve stability required

1. Source gap
    - Favours ion transmission efficiency in the (low) m/z range for $\delta^{13}C$ and $\delta^{15}N$
    - No cost to resolution

2. Prefilter
    - Improves ion transmission efficiency and measurement stability
    - No cost to resolution

3. Rod bias
    - Certain combinations of rod bias and ion injection energy can improve transmission without compromising resolution

CONCLUSIONS AND FURTHER WORK

1-500 Da portable QMS

- Each method independently yields gains
  - Relevance of the post-filter?
- Challenge: thread the approaches together
  - Optimal design of a small footprint QMS
  - High-fidelity simulation is key to this goal
- Combine with dual inlet miniaturisation for a portable IR-QMS system for onsite IRMS for
  - Environmental monitoring (VOCs), volcanology, archaeology, paleobiology, and geochronology

IMAGE CREDITS

Oil burning - http://mansfieldgaswellawareness.weebly.com/industry-news.html

Worker taking readings - https://www.ventia.com/

Laboratory IRMS - https://www.marine.usf.edu/research/facilities-and-equipment/stable-isotope-ratio-mass-spectrometry-facility/

FT-ICR - https://www.gfz-potsdam.de/en/section/organic-geochemistry/infrastructure/ft-icr-ms/

MALDI-TOF – https://www.bruker.com/products/mass-spectrometry-and-separations/maldi-toftof.html

Orbitrap - https://www.thermofisher.com/order/catalog/product/IQLAAEGAAPFALGMAZR

AMS - http://www.pelletron.com/products/accelerator-mass-spectrometry-ams-systems/

QMF - https://www.henniker-scientific.com/products/instruments/gas-phase-chemistry/high-resolution-quadrupole-mass-spectrometers

[all other illustrations: authors]

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- Peter Chaisty and Milos Dragovic (Cyionics, UK)
- Dr. Neil France (Q-Technologies, UK)

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THANK YOU! QUESTIONS?

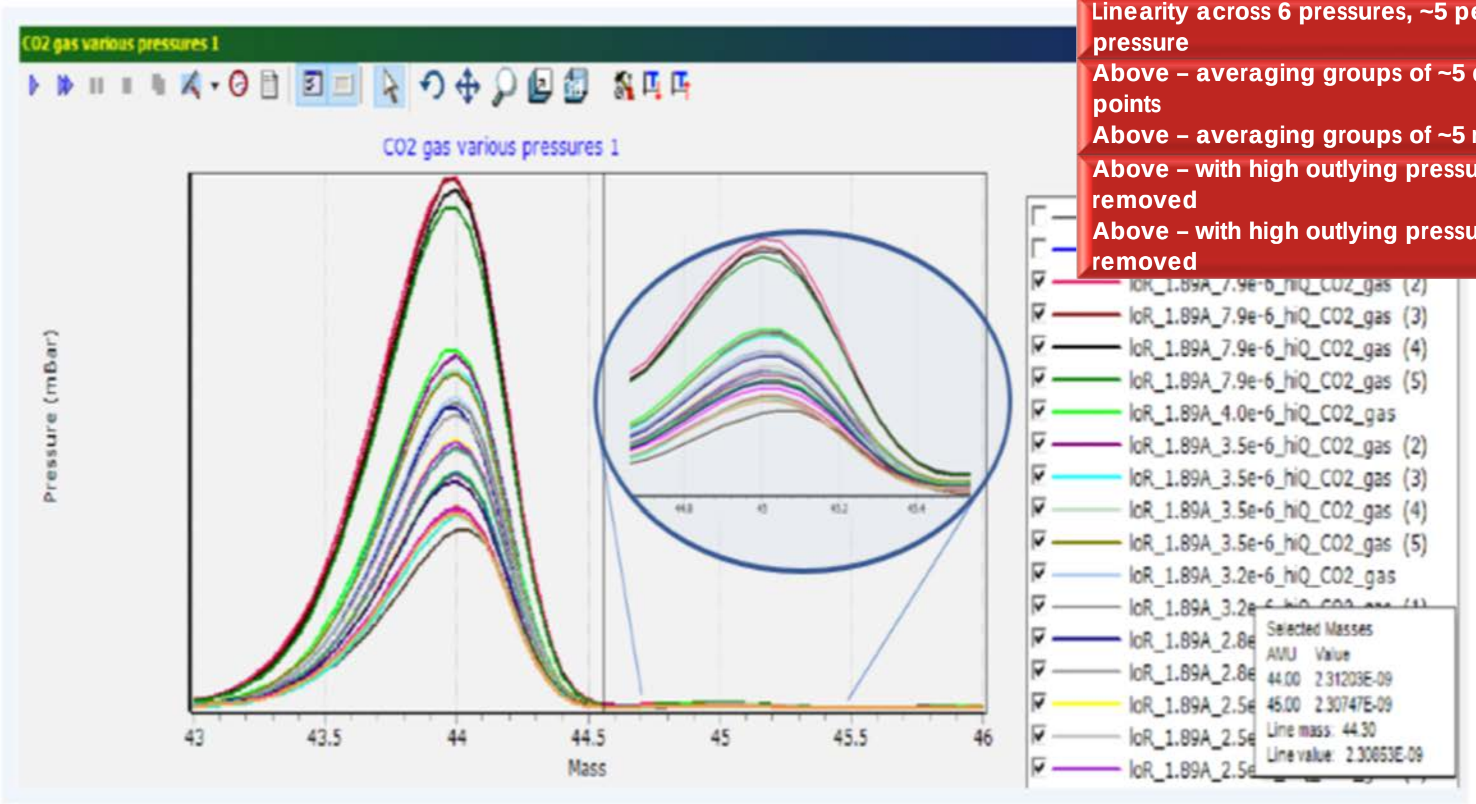
EXTRA SLIDES IF REQUIRED

- 1st: for background / reminder of HySEM-80 early raw d13C results without prefilter, without crimped capillary, etc. (From HEMS last yr)
- 2nd: for some old VapourSense results on N2 isotope stability – if required to satisfy the abstract. (These were presented at ASMS 2017 and HEMS last yr)
- Both could go before slide 11

- PS if preferred,: Slide 11 could be moved to be placed after slide 3 before getting into the main approaches in today's presentation

STABILITY AND LINEARITY – EARLY RESULTS: SINGLE FILTER *HYSEM-80*

CO_2 cylinder gas	Pressure range (Torr)	Mass 45/44 standard deviation	Predicted $\delta^{13}C$ standard deviation
Linearity across 6 pressures, ~5 per pressure	$7.9 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000252	22.4‰
Above – averaging groups of ~5 data points	$7.9 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000159	14.1‰
Above – averaging groups of ~5 ratios	$7.9 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000122	10.9‰
Above – with high outlying pressure removed	$3.6 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000089	7.84‰
Above – with high outlying pressure removed	$3.6 \times 10^{-6} – 1.6 \times 10^{-6}$	0.000090	7.99‰



Measurements from line 1 of Table 1. Six clear groups can be discerned in the mass 44 peak (= mostly $^{12}CO_2$) corresponding to 6 reducing pressure bands of introduction of cylinder CO_2 gas to the needle valve inlet of the portable QMS. The first four of these can be clearly discerned on the inset (mass 45 = ~93% $^{13}CO_2$).

- Need turbulent flow at inlet
- Standard to use a capillary
- Reynold's number: $Re = \frac{\bar{v}D\rho}{\mu}$

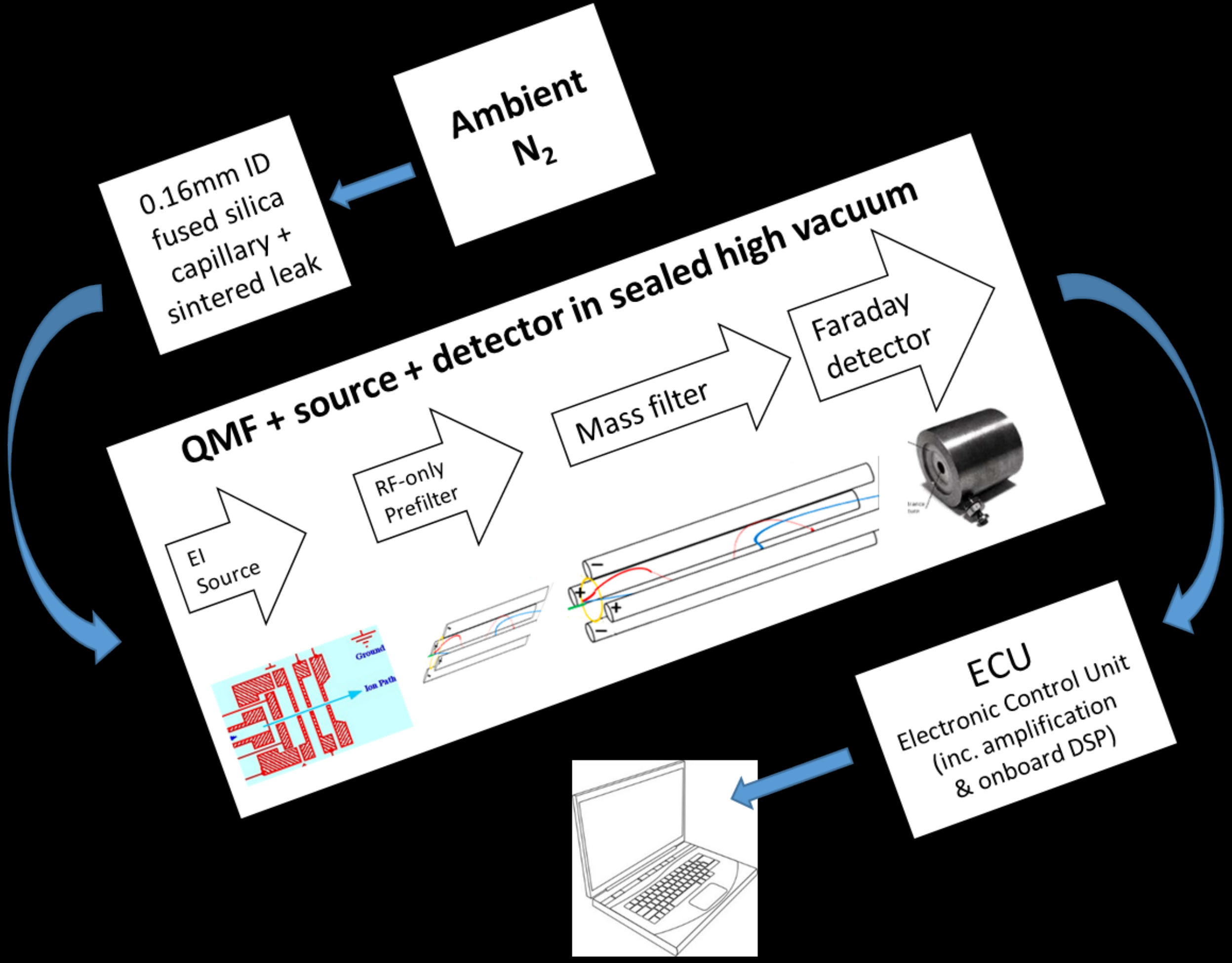
  $v = mean\ velocity$, $\rho = gas\ density$
  $D = vessel\ diameter$, $\mu = gas\ viscosity$

- Re needs to exceed critical value > ~2000 (ideally higher)… 0.15mm I.D. capillary → crimped

STABILITY – PRIOR VAPOURSENSE-500 RESULTS **(N_2)**

- Peak-jumping mode (MIM)
- Sample not pressurised
- Capillary not standard
- Sintered leak may cause fractionation
- 29/28 signal is surprisingly stable despite non-ideal setup

VapourSense-500, ambient N_2 MIM mode (peak jumping)	**m/z 29/28 stand. dev. (1σ)**
Stability across 247 measurements (34-minute period)	**0.0000501**
Above – final 37 measurements only (5-minute period)	**0.0000275**



METHODS

Simulations in x, y, z and time supported by experimental measurements