

A Review of Novel Instrumentation for Matrix Independent Ultratrace Analysis of Radionuclides using Collinear Resonance Ionisation Spectroscopy (CRIS)

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Abstract. The CRIS setup at CERN-ISOLDE is a high resolution laser spectroscopy experiment that is used to characterise exotic radionuclides with very low production rates. Acquisition of hyperfine spectra enable nuclear spins and precise values of nuclear magnetic dipole and electric quadrupole moments to be determined. The high sensitivity of the CRIS technique combined with the high selectivity make it an ideal candidate for quantitation of analytes in complex matrices. This review article reports on novel instrumentation under development at the University of Manchester, utilising the CRIS technique for targeted matrix independent ultra-trace analysis.

1 CRIS Experiment at CERN-ISOLDE

The CRIS experiment at CERN-ISOLDE was first reported in 2013 and uses laser spectroscopy to measure fundamental nuclear properties through acquisition of hyperfine spectra, from which nuclear observables can be extracted [1]. In this way, nuclear moments, relative charge radii and nuclear spins can be determined without relying on assumptions from theoretical models when comparing nuclear properties of isotopes of the same element. It is possible to observe how the shape of the nucleus changes with the addition or subtraction of neutrons.

The CRIS technique combines the high resolution of collinear laser spectroscopy (CLS) with the high sensitivity and efficiency of resonant ionisation spectroscopy (RIS).

The current configuration of the CRIS setup at ISOLDE allows exotic radionuclides to be studied, as well as stable isotopes using a laser ablation source [2]. Exotic radionuclides are produced by impact of the CERN PSBooster proton beam (1.4 GeV) onto the On-Line Mass Separator (ISOLDE) UC_x target. Radionuclides diffuse out of the target, and the resulting beam is mass separated to select the isotope of interest, collisionally cooled and bunched using a gas-filled radiofrequency linear Paul trap and accelerated to 30-50 keV, ready for delivery to the CRIS beam line. Accelerating the ions increases the selectivity of the technique compared with in-source RIS by introducing a kinematic frequency shift of spectral lines for different isotopes.

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The bunched ion beam is neutralized in flight using a heated charge exchange cell loaded with alkali metal vapor, after which any remaining charged species are deflected off axis.

The resulting atom bunches are overlapped with one or more laser beams and synchronised with the laser duty cycle in order to maximise efficiency. The excitation laser frequency is scanned across the electronic transition under investigation, exciting the atoms, which may then be ionized using an additional laser or an electric field. The ions are deflected off axis and detected by an ETP MagneTOF detector. The laser-atom interaction region is maintained at $\sim 10^{-9}$ mbar in order to minimise interference from collisional activated ionization. Recent additions to the beamline include a set of field ionization grids post interaction region, for the ionization of Rydberg atoms [5].

The CRIS experiment at CERN-ISOLDE has successfully completed campaigns on elements of various exotic radionuclei including francium [1], copper [4], radium [6], indium [7], and potassium [8, 9]. More recently isotope shifts of radium monofluoride molecules have been determined [10].

CRIS has performed measurements with short lived nuclei and exotic beam production rates low as 10 atoms per second. Moreover, reduction of collisional background due to interference species by 7 orders of magnitude has been demonstrated [4].

The high sensitivity and selectivity of the CRIS technique allow for its application to both fundamental nuclear physics studies and challenging analytical chemistry based assays.

2 CRIS Experiment at Manchester

Quantitative, label free elemental analysis is often compromised by sample matrix effects. The response of the analyte with most techniques is either enhanced or suppressed by the chemical environment that makes up the remainder of the bulk material (sample matrix). Various strategies exist that endeavor to mitigate these matrix effects. These can include additional sample preparation procedures that can remove matrix interference. Alternate methods of matrix independent quantitation often involve ionization and subsequent quantitation of the analyte in the gas phase. Matrix interference is often significantly reduced when ionising neutrals in the gas phase.

With kinematic isotope separation as well as mass separation with magnets, the capability to measure atomic transitions with linewidths of 25 MHz [11], and demonstrated sensitivities of 10s of atoms per second [4], the CRIS technique enables a specific regime for targeted analysis with matrix independent ultra-trace limits of detection. A CRIS beamline is under development in the Photon Science Institute at the University of Manchester for this purpose. The configuration of the instrument is similar to that at CERN-ISOLDE, incorporating mass selection of the analyte followed by resonant excitation and ionisation, which facilitates additional selectivity above and beyond what is possible with nominal mass separation. Multiple experiments will be carried out on the CRIS instrument in Manchester, which are described in the following sections. Depending on the application, the instrumentation may employ either electron ionisation (EI), electron cyclotron resonance (ECR) or inductively coupled plasma (ICP) as the ion source.

The ion beam is accelerated to 3 - 5 keV and passed through a series of steering and focusing optics. In order to make the experimental set up as compact as possible, the

Manchester CRIS beamline is on 2 levels. Ions are produced at one end of the lower beamline and travel through a set of electrodes to steer and focus the beam onto the top level. A linear Paul trap cooler buncher based on previous work [13, 14] (figure 1 RFQcb), currently under development, will be installed to produce a bunched beam compatible with the duty cycle of the laser system. The ion beam is focused through a charge exchange cell where it is neutralised in flight. Ions that are not neutralised are deflected out of the beam. The charge exchange cell is heated to 513 K and uses sodium vapour as the charge exchange media.

The excitation laser or lasers are steered into the beamline on the top level, overlapping with the fast atom beam. Atoms neutralised into the chosen spectroscopic state will be resonantly excited to a state from which they will be ionised. The ionisation step will be provided by one of two methods. For the first method, the 532 nm output of a Nd:YAG laser will be steered through the upper beamline to ionise the excited atoms. For the second method, potentials will be applied to 3 wire grids, mounted on printed circuit boards and spaced 4 mm apart, which are positioned in the path of the neutral beam. The resulting electric field will ionise Rydberg atoms passing through the region by field ionisation [5].

An electron multiplier detector is positioned offaxis. A final pair of deflectors steer ions into the electron multiplier, where they will be counted. The resulting signal will be gated on the laser pulse timing. Later iterations of the CRIS beamline will utilise a multicollector magnetic sector for mass separation.

2.1 Detection of Krypton-85

^{85}Kr is a radioactive noble gas present in the atmosphere. Although a small amount of ^{85}Kr is produced naturally through the interaction of cosmic neutrons with stable isotopic neighbour ^{84}Kr , the majority originates from anthropogenic sources. As a fission product, ^{85}Kr is formed in nuclear reactors. Unless the fuel cladding is damaged, the ^{85}Kr formed is retained in spent fuel rods, which are usually kept in storage for a minimum of 6 months after use in order to reduce their activity. An increase in the atmospheric concentration of ^{85}Kr in the vicinity of a storage facility can indicate a leak in fuel containers. When spent fuel rods are reprocessed, most of the ^{85}Kr is released into the atmosphere, and is difficult to contain. Considering these implications, accurate ^{85}Kr measurement also has applications in nuclear security, as a spike in local atmospheric concentration could indicate the presence of an undeclared reprocessing facility [12].

^{85}Kr is present in the atmosphere with an isotopic abundance of 10^{-12} and atmospheric concentration of 10^{-18} . It is therefore necessary that ^{85}Kr detection requires both high sensitivity and mass resolution (abundance sensitivity) to be able to resolve the ^{85}Kr signal over the much larger ^{84}Kr component, as well as distinguishing it from any isobaric interference. After initial proof of principle studies the beamline will be optimised for the measurement of $^{85}\text{Kr}/^{84}\text{Kr}$ isotopic ratios.

For initial studies, CRIS will be performed on argon atoms. In the current configuration, argon gas is injected into an EI ion source at a rate of 1 mL min^{-1} , where singly-charged argon ions are produced and extracted through 4 electrostatic lenses. Currently, argon beams of around $0.25 \mu\text{A}$ are measured immediately after extraction. Simulations based on electron-capture cross section calculations [15] have demonstrated that after neutralisation by sodium vapour, the metastable $4s^2_{[3/2]}0$ state in argon will be

42.6% populated. From this state, argon atoms can be excited to high-lying Rydberg states through 1-photon absorption of 300 nm light [16].

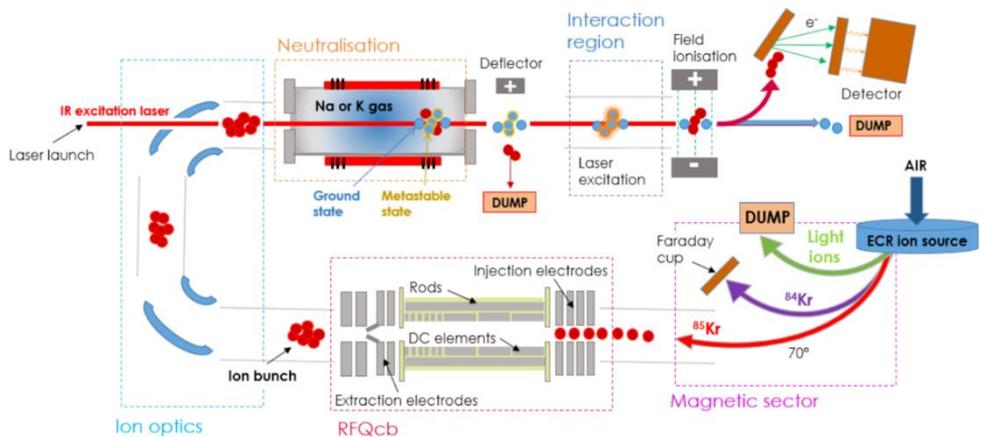


Fig. 1. Manchester CRIS setup with ECR gas inlet configured for ^{85}Kr analysis with multi-collector magnetic sector

2.2 Radiocarbon Dating

Accelerator Mass Spectrometry (AMS) is the industry standard method for radiocarbon dating applications. When used for radiometric dating, AMS employs a multi-collector detector array for isotope ratio mass spectrometry. The most common method of sample introduction involves complete combustion of the sample in pure oxygen to evolve carbon dioxide gas; this is then graphitised and loaded into a metal target alongside reference materials used as external standards for quantification. A primary caesium ion gun is directed at the samples to produce secondary negative carbon ions which are then accelerated to the stripper in the centre of a tandem accelerator. The stripper removes the negative charge and reduces the negative carbon ions to a triply charge positive carbon ion which are then accelerated out of the tandem accelerator for subsequent mass selection. The carbon ions are resolved according to their m/z ratio in order to resolve the ^{12}C , ^{13}C and cosmogenic ^{14}C isotopes. The relative isotopic abundances may be used to calculate the date at which biological sample deceased. when using relatively small accelerating potentials on AMS instruments, it is not always possible to perform radiometric dating of larger cosmogenic radionuclides such as ^{26}Al or ^{36}Cl .

The CRIS beamline in Manchester will be optimised for the detection of the low abundance ^{14}C isotope, in order to perform radiocarbon dating. Samples submitted for carbon dating analysis are first combusted in pure oxygen using a flash gas chromatograph. The combustion gases are then separated on column, reducing the nitrogen background by a factor of approximately 10^6 . Further suppression and removal of nitrogen gas interference is achieved by means of a cryogenic concentrator. The eluting carbon dioxide combustion fraction is diverted post column into a cryogenic trap cooled to 77 K using a 10-port Valco switching valve. The carbon dioxide elutes in a helium carrier gas with a flow rate of 120 mLmin^{-1} . Once trapped the solid carbon dioxide is ready for analysis. The 10-port valve

switches an additional helium flow set at 1 mLmin^{-1} into the trap which is then heated to room temperature. The carbon dioxide sublimates and is swept into an ECR ion source to be ionised and fragmented into singly charged positive carbon ions, which will ultimately be delivered to the main beamline. The CRIS setup will be operated in the same way described earlier for the ^{85}Kr analysis, employing the same multi-collector magnetic sector mass analyser used for the ^{85}Kr application depicted in figure 1. The magnet would be tuned for the separation of the carbon isotopes, and the lasers will be tuned for resonant excitation of ^{14}C .

The application of CRIS to radiometric dating applications offers advantages when compared to AMS techniques. One advantage is that the lasers may be tuned to be on resonance with almost any element from across the periodic table, which would allow for radiometric dating of ^{26}Al and ^{36}Cl . Additionally, the use of an ECR ion source and direct analysis of the carbon dioxide from combusted samples negates the need for a graphitisation step. This reduces this significant bottle neck often experienced when using AMS techniques, as the graphitisation process itself introduces additional experimental errors associated with sample preparation. The capacity of the ECR ion source to produce beams of $> 1 \text{ mA}$ will also significantly speed up the radiometric dating process.

2.3 Hyphenation of CRIS with ICP-MS

The hyphenation of the CRIS technique to industry standard ultra-trace analytical techniques, such as inductively coupled plasma mass spectrometry (ICPMS) offers many advantages including the ease of integration with existing workflows. CRIS has the potential to offer additional sensitivity and selectivity for challenging applications that require limits of currently not available even with state-of-the-art tandem mass analyser based ICP-MS/MS instrumentation.

Many applications of radioisotope analysis in the field of nuclear decommissioning require limits of detection not currently achievable with the latest instrumentation, but would be made possible with ICP-MS-CRIS. In particular, this novel technique will be used for the quantification of ^{90}Sr , which is a high yield fission product and is continuously created in civil nuclear power plants. The long half-life, environmental mobility and ability of ^{90}Sr to concentrate within the food chain make this an important radionuclide for nuclear decommissioning and waste characterisation.

In many applications, such as processing plant waste sentencing, ^{90}Sr levels are inferred by determining a gamma spectroscopy “fingerprint” for a substrate and then measuring concurrently and reliably produced ^{137}Cs . However, the differing partitioning of ^{90}Sr and ^{137}Cs in the environment, particularly in soil and groundwater, invalidates any ‘fingerprinting’ and both isotopes must be measured independently. The existing method for ^{90}Sr quantification comprises of Cherenkov counting of the daughter isotope ^{90}Y . This requires complete chemical separation of ^{90}Sr and a >20 day grow in period of the ^{90}Y daughter isotope which constitutes a major bottleneck in the analysis of ^{90}Sr . At the present time only the Cherenkov counting method is accredited and sensitive enough to detect ^{90}Sr present in environmental samples which are set with an upper limit of 0.5 BqL^{-1} in groundwater and 8 Bqkg^{-1} in soil in the United Kingdom.

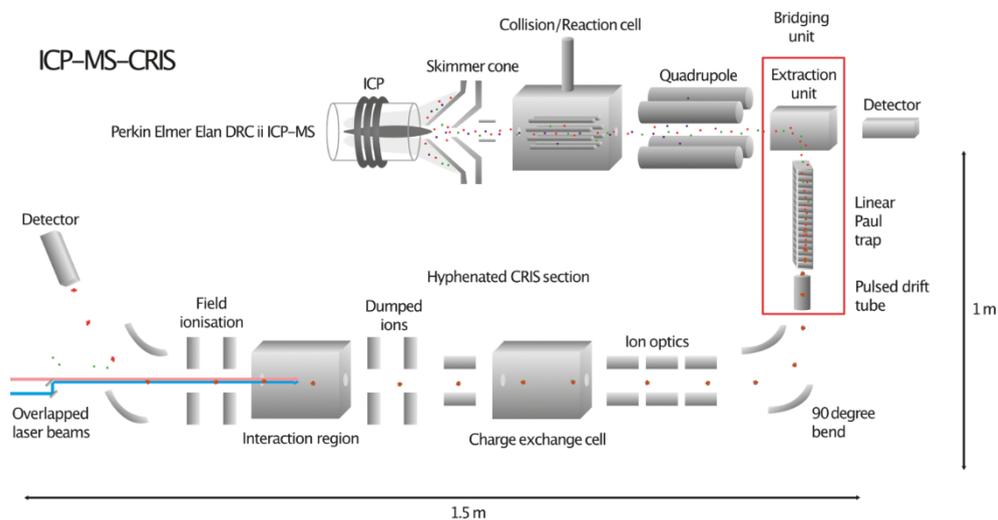


Fig. 2. Manchester CRIS setup with hyphenation to ICP-MS instrumentation for ICP-MS-CRIS

As the nuclear decommissioning programme accelerates, the ability to characterise larger volumes and sample numbers requires a cost-effective solution. Additionally, the practical requirements of site characterisation, remediation and verification/validation demand a quantification technique with a rapid capability, ideally with a turnaround time of a few hours. ICP-MS-CRIS has the capacity to fulfil these requirements.

In addition to ^{90}Sr , there also exists a range of short-lived isotopes which are important within the decommissioning process that also require multi-stage chemical separation before they can be measured.

The hyphenation of ICP-MS with CRIS will be achieved via a bridging unit between an ICP-MS instrument and a CRIS beamline. The bridging unit will consist of an ion extraction unit, linear Paul trap and ion optics. The ion extraction unit is comprised of two ion carpets and three repeller plates that divert ions leaving the ICP-MS quadrupole mass analyser through a 90° bend into the linear Paul trap. The ion carpet is made up of 24 concentric circular rings originating from a 2 mm entrance aperture, and a series of rectangular repeller plates shown in figure 3. The ion extraction unit will be located in a 46 x 123 mm region between the ICP-MS quadrupole and the detector.

The carpet operates with a DC potential gradient, known as the drift potential, applied across the ring electrodes to guide ions towards the aperture and into the linear Paul trap. When operating in the 10^{-2} mbar range, the buffer gas reduces the ion kinematics.

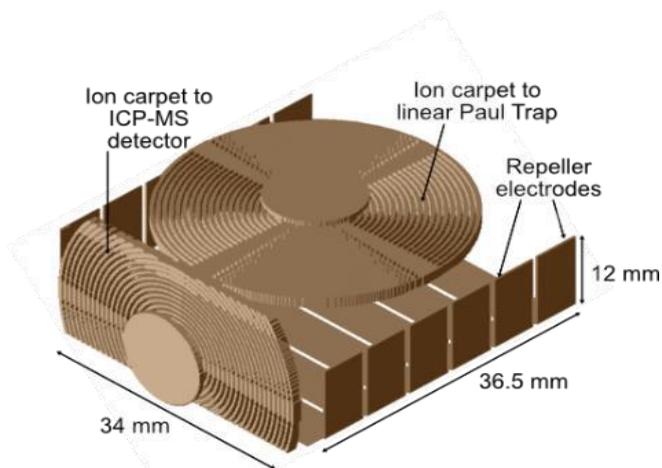


Fig. 3. SIMION 3D representation of the ion extraction unit. A series of repeller plates perpendicular and opposite to two ion carpets.

An RF potential applied to a set of electrodes causes the ions to hover and oscillate over the carpet while a DC potential directs the ions towards the aperture.

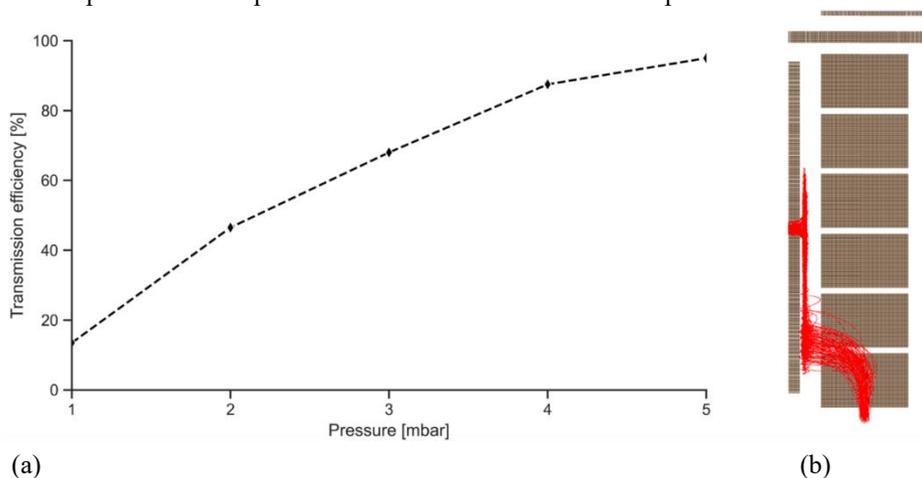


Fig. 4. (a) Simulated ion transmission in the mbar range (b) Example of ion motion under applied DC and RF potentials at 5 mbar.

SIMON simulations, using m/z 90 to represent ^{90}Sr , indicate a near 100% ion transmission efficiency in the mbar region; as exemplified in Figure 4. At pressures below 10^{-2} mbar, the DC potential begins to dominate as the RF potential diminishes and becomes negligible due to the reduced buffer gas pressure. As the linear Paul trap has an operating pressure of 10^{-2} mbar and is mounted directly onto the extraction unit, the operating pressure of the extraction unit will be between 10^{-6} mbar (ICP-MS operating pressure) and 10^{-2} mbar.

Simulations at the upper limit of operating pressure, shown in Figure 6, indicate an ion transmission efficiency of around 40-45%, however, by optimising the extraction unit geometry, the anticipated transmission efficiency will likely increase.

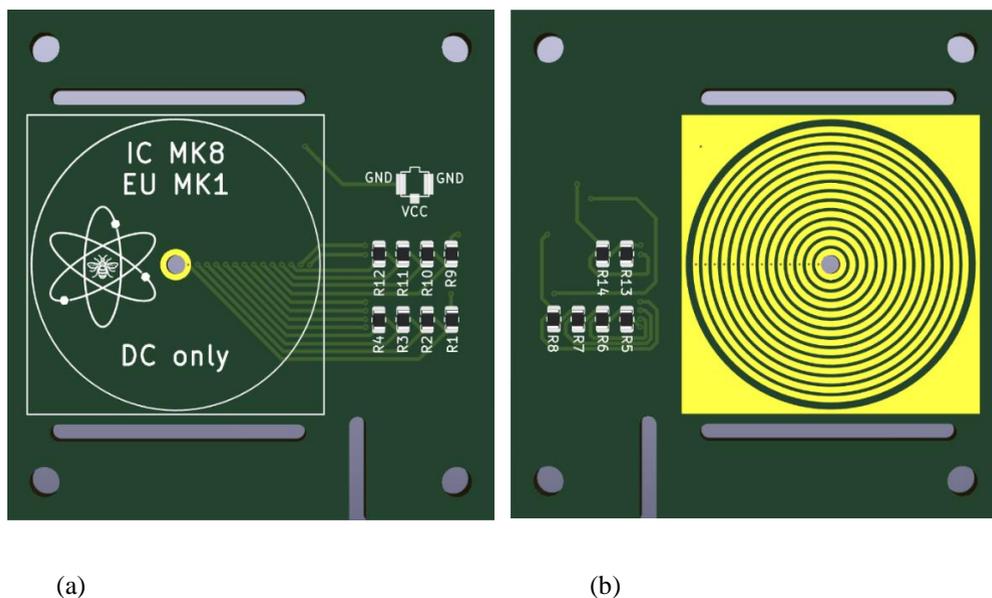


Fig. 5. 3D rendering of the top (a) and bottom (b) panels of the ion carpet which extracts the ions that traversed through the ICP-MS quadruple.

The ion extraction unit will be constructed using printed circuit boards.. The extraction unit will be tuned to transmit ions of various m/z values. The top and bottom panels of the extracting ion carpet is shown in Figure 5 (a) and (b) with a resistor chain determining the potential on each ring electrode. The planar linear Paul trap along with the ion extraction unit, will be investigated to determine its suitability for the hyphenation of ICP-MS with CRIS.

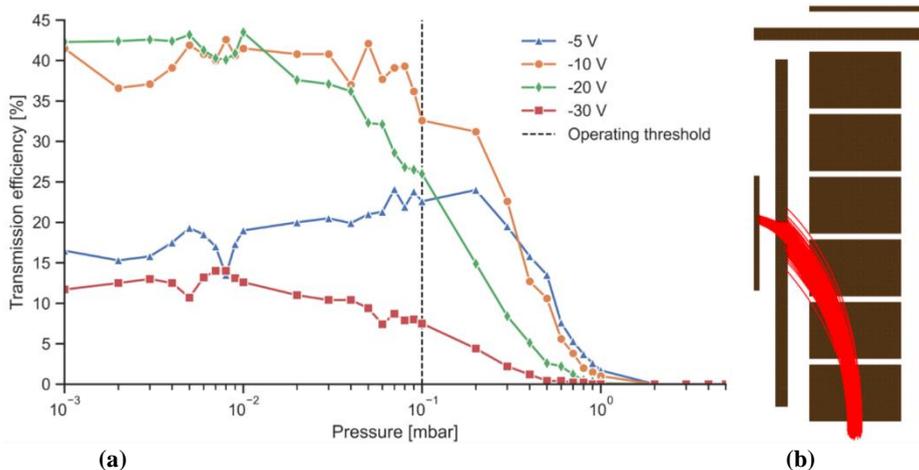


Fig. 6. (a) Simulated ion transmission in the mbar range (b) Example of ion motion with only an applied DC potential at 1×10^{-2} mbar.

References

1. K. T. Flanagan, K. M. Lynch, J. Billowes, M. L. Bissell, I. Budincevic, T. E. Cocolios, R. P. de Groote, S. De Schepper, V. N. Fedosseev, S. Franchoo, R. F. Garcia Ruiz, H. Heylen, B. A. Marsh, G. Neyens, T. J. Procter, R. E. Rossel, S. Rothe, I. Strashnov, H. H. Stroke, and K. D. A. Wendt. *Phys. Rev. Lett.* **111**, 212501 (2013)
2. R. F. Garcia Ruiz, A. R. Vernon, C. L. Binnersley, B. K. Sahoo, M. Bissell, J. Billowes, T. E. Cocolios, W. Gins, R. P. de Groote, K. T. Flanagan, A. Koszorus, K. M. Lynch, G. Neyens, C. M. Ricketts, K. D. A. Wendt, S. G. Wilkins, and X.F. Yang. *Phys. Rev. X* **8**, 041005 (2018)
3. S. Rothe, T. D. Goodacre, D. Fedorov, V. Fedosseev, B. Marsh, P. Molkanov, R. Rossel, M. Seliverstov, M. Veinhard, and K. Wendt, *Nucl. Instrum. Methods Phys. Res., Sect. B* **376**, 91, (2016)
4. R. P. de Groote, J. Billowes, C. L. Binnersley, M. L. Bissell, T. E. Cocolios, T. Day Goodacre, G. J. Farooq-Smith, D. V. Fedorov, K. T. Flanagan, S. Franchoo, R. F. Garcia Ruiz, Á. Koszorus, K. M. Lynch, G. Neyens, F. Nowacki, T. Otsuka, S. Rothe, H. H. Stroke, Y. Tsunoda, A. R. Vernon, K. D. A. Wendt, S. G. Wilkins, Z. Y. Xu, and X. F. Yang. *Phys. Rev. C* **96**, 041302(R) (2017)
5. A. R. Vernon, C. M. Ricketts, J. Billowes, T., E. Cocolios, B. S. Cooper, K. T. Flanagan, R. Garcia Ruiz, F. P. Gustafsson, G. Neyens, H. A. Perrett, B. K. Sahoo, Q. Wang, F. J. Waso, and X. F. Yang. *Sci. Rep.* **10**, 12306 (2020)
6. K. M. Lynch, S. G. Wilkins, J. Billowes, C. L. Binnersley, M. L. Bissell, K. Chrysalidis, T. E. Cocolios, T. Day Goodacre, R. P. de Groote, G. J. Farooq-Smith, D. V. Fedorov, V. N. Fedosseev, K. T. Flanagan, S. Franchoo, R. F. Garcia Ruiz, W. Gins, R. Heinke, Á. Koszorus, B. A. Marsh, P. L. Molkanov, P. Naubereit, G. Neyens, C. M. Ricketts, S. Rothe, C. Seiffert, M. D. Seliverstov, H. H. Stroke, D. Studer, A. R. Vernon, K. D. A. Wendt, and X. F. Yang. *Phys. Rev. C* **97**, 024309 (2018)
7. B. K. Sahoo, A. R. Vernon, R. F. Garcia Ruiz, C. L. Binnersley, J. Billowes, M. L. Bissell, T. E. Cocolios, G. J. Farooq-Smith, K. T. Flanagan, W. Gins, R. P. de Groote, Á. Koszorus, G. Neyens, K. M. Lynch, F. Parnefjord-Gustafsson, C. M. Ricketts, K. D. A. Wendt, S. G. Wilkins, and X. F. Yang. *New J. Phys.* **22**(1), 012001 (2020)
8. Á. Koszorus, X. F. Yang, J. Billowes, C. L. Binnersley, M. L. Bissell, T. E. Cocolios, G. J. Farooq-Smith, R. P. de Groote, K. T. Flanagan, S. Franchoo, R. F. Garcia Ruiz, S. Geldhof, W. Gins, A. Kanellakopoulos, K. M. Lynch, G. Neyens, H. H. Stroke, A. R. Vernon, K. D. A. Wendt, and S. G. Wilkins. *Phys. Rev. C* **100**, 034304 (2019)
9. Á. Koszorus, X. F. Yang, W. G. Jiang, S. J. Novario, S. W. Bai, J. Billowes, C. L. Binnersley, M. L. Bissell, T. E. Cocolios, B. S. Cooper, R. P. de Groote, A. Ekström, K. T. Flanagan, C. Forssén, S. Franchoo, R. F. Garcia Ruiz, F. P. Gustafsson, G. Hagen, G. R. Jansen, A. Kanellakopoulos, M. Kortelainen, W. Nazarewicz, G. Neyens, T. Papenbrock, P.G. Reinhard, C. M. Ricketts, B. K. Sahoo, A. R. Vernon, and S. G. Wilkins *Nat. Phys.* , (2021)
10. S. M. Udrescu, A. J. Brinson, R. F. Garcia Ruiz, K. Gaul, R. Berger, J. Billowes, C. L. Binnersley, M. L. Bissell, A. A. Breier, K. Chrysalidis, T. E. Cocolios, B. S. Cooper, K. T. Flanagan, T. F. Giesen, R. P. de Groote, S. Franchoo, F. P. Gustafsson, T. A. Isaev, Á. Koszorus, G. Neyens, H. A. Perrett, C. M. Ricketts, S. Rothe, A. R. Vernon, K. D. A. Wendt, F. Wienholtz, S. G. Wilkins, and X. F. Yang *Phys. Rev. Lett.* , (2021)
11. S. G. Wilkins, K. M. Lynch, J. Billowes, C. L. Binnersley, M. L. Bissell, T. E. Cocolios, T. Day Goodacre, R. P. de Groote, G. J. Farooq-Smith, K. T. Flanagan, S. Franchoo, R. F. Garcia

- Ruiz, W. Gins, H. Heylen, Á. Koszorús, Neyens, H. H. Stroke, A. R. Vernon, K. D. A. Wendt, and X. F. Yang. *Phys. Rev. C* **96**, 034317 (2017)
12. Kalinowski, M. B.(1994). Proceedings of the workshop on the state of measurement technologies for identification of nuclear signatures. EUR17312, pp 67-72
 13. B. S. Cooper, H. A. Perrett, C. M. Ricketts, C. Read, G. Edwards, K. T. Flanagan, J. Billowes, C. L. Binnersley, M. L. Bissell, T. E. Cocolios, R. P. de Groote, G. J. Farooq-Smith, R. F. Garcia Ruiz, W. Gins, Á. Koszorús, G. Neyens, F. P-Gustafsson, H. H. Stroke, A. R. Vernon, K. D. A. Wendt, S. G. Wilkins, and X. F. Yang. *Hyperfine Interact.* **240**, 52 (2019)
 14. C. M. Ricketts, B. S. Cooper, G. Edwards, H. A. Perrett, J. Billowes, C. L. Binnersley, T. E. Cocolios, K. T. Flanagan, R. F. Garcia Ruiz, R. P. de Groote, F. P. Gustafsson, Á. Koszorús, G. Neyens, A. R. Vernon, and X. F. Yang. *Nucl. Instrum. Methods Phys. Res. B* **463**, 375-377 (2020)
 15. A. R. Vernon, J. Billowes, C. L. Binnersley, M. Bissell, T. E. Cocolios, G. J. Farooq-Smith, K. T. Flanagan, R. F. Garcia Ruiz, W. Gins, R. P. de Groote, A. Koszorus, K. M. Lynch, G. Neyens, C. M. Ricketts, K. D. A. Wendt, S. G. Wilkins, and X.F. Yang. *Spectrochim. Acta. B* **153**, 61-83 (2019)
 16. M. Pellarin, *Phys B-At. Mol. Opt.* **21** (23), pp.3833-3849 (1988)