

Mass Spectrometry & Spectroscopy

Development of Novel ICP-MS-CRIS Instrumentation Hyphenating Inductively Coupled Plasma Mass Spectrometry with Collinear Resonance Ionisation Spectroscopy (CRIS)

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Introduction to spectroscopy and Artemis Analytical Ltd

Artemis Analytical Ltd is a spin out company from the University of Manchester that is aiming to commercialise core technologies that were developed by University researchers whilst working at CERN. The novel quantum technologies employed combine or hyphenate mass spectrometric separation with high resolution resonance laser spectroscopy for the ultimate complement of ultra-trace sensitivity with specificity for matrix independent elemental analysis.

The use of spectroscopy for elemental analysis has had an interesting evolution throughout the ages, starting with flame atomic emission experiments conducted by Bunsen back in the 1860's through to inductively coupled plasma atomic emission spectroscopy (ICP-AES). A variety of absorbance techniques and more recently the use of X-rays in the form of particle induced X-ray emission (PIXE) all have their respective niche applications in the analysts tool kit. However, it was not until the invention of inductively coupled plasma mass spectrometry (ICP-MS) that isotopic resolution was possible coupled with significant improvements in sensitivity for ultra-trace elemental analysis. Tandem ICP-MS/MS instrumentation also enabled isobaric resolution through the use of reaction cells.

All analytical techniques suffer to a greater or lesser degree with matrix effects, the measurement of the analyte response is either enhanced or suppressed by the rest of the sample (the matrix). Matrix effects may either be accounted for in the analysis or removed with additional sample preparation steps. Matrix independent measurements are sometimes possible by increasing the selectivity or ideally the specificity of a technique and that is the aim of the new ICP-MS-CRIS technique under discussion.

Characterisation of nuclear waste for low-level waste repository

The United Kingdom's legacy nuclear estate is currently being decommissioned, contaminated equipment and even buildings are assessed and consigned to either low, medium or high-level waste repositories according to the levels of radioactive contamination. Estimates as high as £1 trillion clean-up costs for the civilian nuclear waste alone have been forecast over the next 200 years. The land requires remediation, the various radionuclides present are characterised and quantified to decide on the appropriate waste stream. Ultra-trace measurements or 'boundary assignments' of radionuclides classed as either free release to land fill or low-level waste repository stream requires accurate measurement in order not to occupy valuable space within the low-level waste repository that could otherwise be diverted to landfill.

Strontium-90 is a by-product of the nuclear industry and is one of the most difficult radionuclides to quantify at the required lower limit. It is a beta emitter and poses various issues when released into the environment: its solubility, mobility, and uptake within the biosphere makes monitoring its distribution imperative. To date even the most sensitive tandem quadrupole ICP-MS/MS instrumentation lacks the sensitivity and selectivity required to measure strontium-90 at the level required due to high level isobaric zirconium-90 matrix interference from the soil.

Tandem quadrupole ICP-MS/MS analysis of strontium-90?

If a tandem quadrupole ICP-MS/MS instrument was to be used for the analysis of strontium-90 the instrument is setup for 'on mass' measurement with oxygen in the reaction cell. The first quadrupole is set to m/z 90 for precursor ion selection, all

isobaric ions of the selected m/z will enter the reaction cell. The reaction of $^{90}\text{Sr}^+$ ions with oxygen in the cell is endothermic so no reaction occurs, however, the $^{90}\text{Zr}^+$ reaction is exothermic; $^{90}\text{ZrO}^+$ ions are produced with a 'mass shift' from m/z 90 to m/z 106. The second quadrupole after the reaction cell is also set to m/z 90 so only the unreacted $^{90}\text{Sr}^+$ ions will reach the detector and be measured. As first impressions go it would appear that we have a solution to the zirconium matrix removal issue, however, the efficiency of the ZrO^+ formation is only 99.7% so if the matrix interference is on the order of 100 ppm there will still be a large population of unreacted $^{90}\text{Zr}^+$ ions that will interfere with the measurement of sub ppt level $^{90}\text{Sr}^+$. The current UKAS accredited method employed used liquid scintillation counters, in short, it takes between 20-30 days to measure the concentration of strontium-90 which poses a serious bottleneck in the analytical workflow.

CRIS Collaboration at CERN, characterisation of exotic radionuclei

One possible solution to speeding up analysis times for this application involves the development of a novel analytical technique by hyphenating industry standard ICP-MS technologies with high resolution collinear resonance ionisation spectroscopy (CRIS). The CRIS technique was initially developed at the Isotope mass Separator On-Line Device (ISOLDE) at CERN in Switzerland for the characterisation of exotic radio nuclei formed when the 1.4 GeV proton booster beam is impinged on a uranium carbide target to produce the element under investigation via spallation and fragmentation mechanisms. Various exotic short-lived radioactive isotopes some of which have very low production rates effuse and diffuse out of the target, the ensemble of radioisotopes are then resonantly ionised using lasers and extracted into the beam line. The isotope of interest is mass selected by magnetic sector, collisionally cooled and bunched

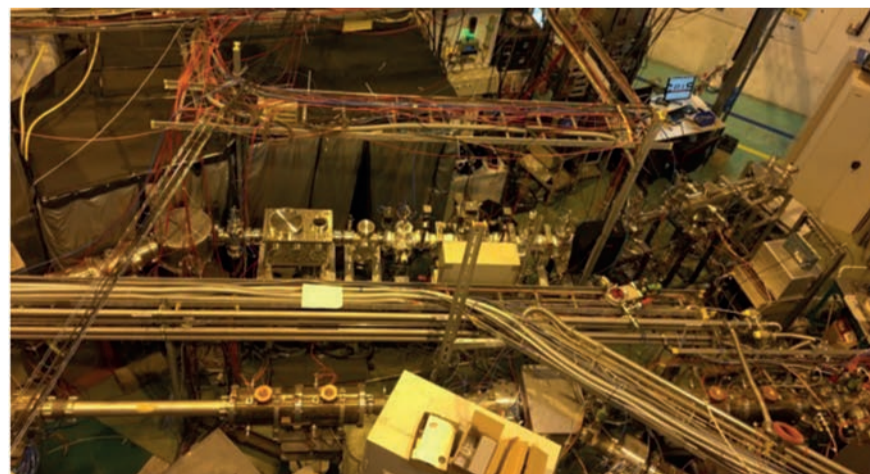


Figure 1: CRIS Collaboration beamline at ISOLDE, CERN.

into microsecond bunches before being accelerated up to 50 keV into the CRIS beamline. The mass selected bunched ion beam containing the isotope under investigation is focused through a charge exchange cell into the laser interaction region, the charge exchange process utilises sodium vapour which neutralises the ion beam in-flight to the ground state. One or more narrow bandwidth laser/s are tuned to be resonant with the isotope under investigation, they are triggered to fire with optimised spatial and temporal overlap with the fast atom beam within the laser interaction region.

The inherently low velocity spread of the fast atom beam when excited by collinearly propagated laser beams enables hyperfine atomic absorbance spectra to be acquired when the laser frequency is scanned across the resonance transition. From the acquired hyperfine structure it is possible to deduce various properties of the nucleus including the nuclear spin and moments as well as the charge radius. When the isotopes are mass selected and bunched they are all accelerated to the same kinetic energy by the linear Paul trap, the different isotopes will all be accelerated to a different mass dependent velocity, this Doppler or kinematic shift facilitates isotopic resolution with unrivalled abundance sensitivity which gives an additional dimension of selectivity in addition to mass selection.

It has been demonstrated by the CRIS collaboration at ISOLDE, CERN that it is possible to measure hyperfine spectra of exotic short-lived radio nuclei even when present in an isobaric matrix interference that is more than 10^7 times in abundance.

CRIS instrument development, Research and Development of ICP-MS-CRIS in Manchester

The CRIS instrumentation being developed by Artemis Analytical at the University of Manchester is based on 'targeted analysis' rather than the nuclear characterisation experiments performed at ISOLDE, CERN. In short the lasers are tuned to be on-resonance for maximum sensitivity rather than scanning them to acquire hyperfine spectra.

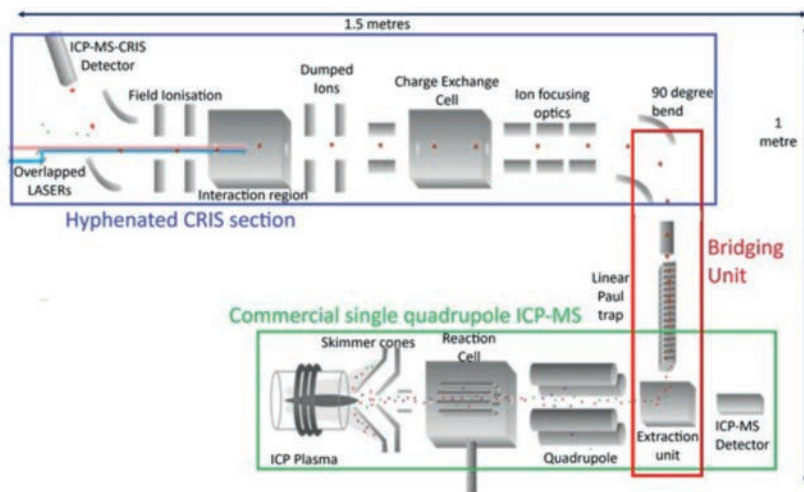


Figure 2: Schematic of the ICP-MS-CRIS instrumentation.

The development process for the ICP-MS-CRIS instrument in Manchester has been realised with sustainability as one of the key design considerations. The ICP-MS donor instrument is an up-cycled Perkin Elmer Elan DRC II ICP-MS and nearly all of the ultra-high vacuum stainless steel vacuum chambers have been re-used or up-cycled from no longer functional donor instruments. The RF linear Paul trap used to collisionally cool and bunch the ion beam has been prototyped using 3D printed PLA components that are inherently compatible with high vacuum systems. The RF generator used is open source and is a modified version of the Wisconsin Oscillator which costs less than £30 per unit. The use of spark plugs for high voltage feedthroughs has also kept the cost down and enabled the project to run on budget.

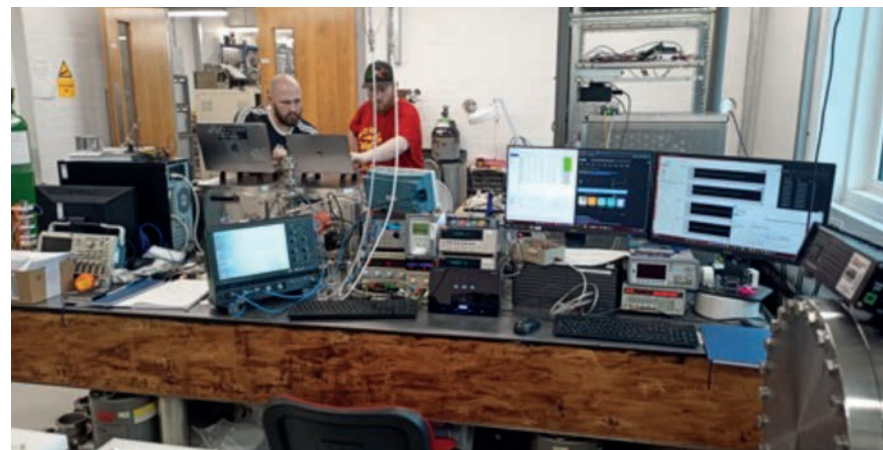


Figure 3: RF only linear Paul trap test rig used to bunch the ion beam.

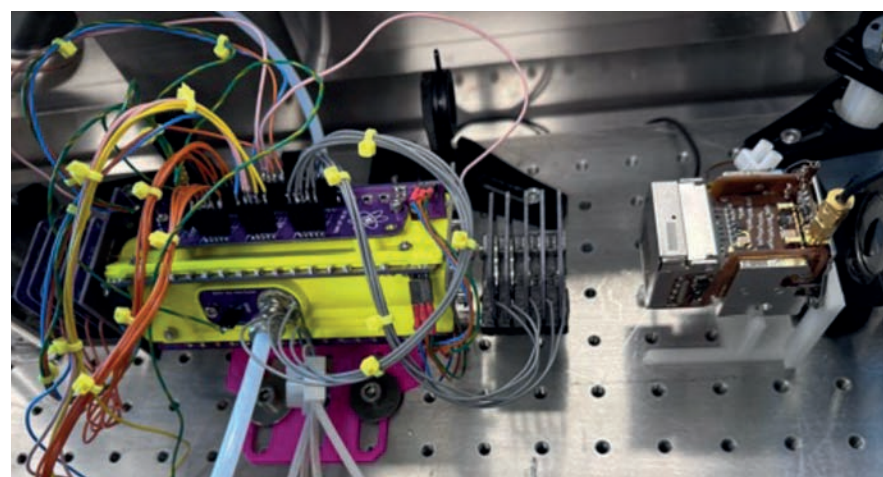


Figure 4: 3D printed first generation of linear Paul trap.

As far as the instrument operator is concerned there should not be too much in the way of additional training required, we aim to provide a turnkey solution and are already in talks with ICP-MS instrument vendors who can assist us with the seamless integration within their existing instrumentation, software and analytical workflows. The operator would essentially choose a CRIS method for the element/isotope of interest which would then run a single quadrupole mass analyser as normal in selected ion monitoring (SIM) mode. There is an additional bridging unit which interfaces the ICP-MS with the CRIS technique which consists of an RF carpet that would then extract the mass selected ions orthogonally and into the RF linear Paul trap. The trap collisionally cools the beam and bunches it (trap/release) to match the repetition rate of the laser system. The bunched beam is accelerated and neutralised in flight before entering the laser interaction region where it is overlapped collinearly with the resonant laser beam tuned for the excitation of strontium-90. The excited atoms are then ionised using either a second non-resonant laser or field ionisation grids.

Conclusion

The main advantage of the ICP-MS-CRIS system is that it can be applied to almost any element across the periodic table. The laser system would have to be tuned to be resonant with respect to the analyte of interest, multiple lasers could be embedded within the system to give multi-element ICP-MS-CRIS capabilities with unrivalled speed of analysis, sensitivity and selectivity. The CRIS technique may also be used in place of accelerator mass spectrometry (AMS) for ultra-trace high abundance sensitivity isotope ratio mass spectrometry applications such as carbon dating which is also currently under development.