

Photoionization Workshop Report

“Bridging the Gap between Academic and Industrial Research”

67th ASMS Conference on Mass Spectrometry and Allied Topics, Atlanta, GEORGIA

Monday, June 3rd, 5:45 – 7:00 pm, Room A303

Organized by: Eleanor Riches, Sven Ehlert and Matthias Lorenz

Approx. Attendance: 40 – 50 people

Organizational matters

- We feel that two years is too short for the workshop chair to understand fully all the procedures and requirements for creating a successful interest group workshop so we propose that we will go to a three-year cycle with the replacement chairperson acting as an assistant in preparation for assuming the role in the following year.
- Next year’s interest group coordinators will be Sven Ehlert and Matthias Lorenz, assisted by Luke Hanley.
- The interest group supports the oral session “Fundamentals: Photoionization and Photodissociation” for the ASMS 2020
- There was a huge progress in 2019 in the selection of the PI session contributions to cover the diversity in the field.
- Chengli Zu, from Corteva, indicated his interest in being a future workshop coordinator.

Content: Under the topic “Bridging the Gap between Academic and Industrial Research”, this year’s workshop opened with two short presentations, one from an academic environment and one from industry.

Dr. Christopher Rüger (University of Rouen, France) presented on his collaborative work with TOTAL Refining & Chemicals (France) in an industrial setting using a commercial APPI source for the analysis of complex petrochemical compound mixtures, including the comparison between ESI and APPI for compound class coverage.

Dr. Giles Edwards (University of Manchester, UK) talked about his research in an academic environment on the development of a novel analytical technique based on Colinear Resonance Ionization Spectroscopy (CRIS) combined with an ICP-MS for the quantitation of ⁹⁰Sr for the purpose of nuclear waste decommissioning. The key message was that hyphenation of CRIS to the back end of an ICP-MS for industry will save analysis time, capital outlay and lest we forget an increase in selectivity and sensitivity

Both presenters put an emphasis on the role of photoionization in their research and contributed with questions to the discussion. The talks illustrated the different needs and possibilities in the respective setting, e.g. for the development and utilization of complex instrumentation. This enabled to stimulate a vivid discussion about the challenges posed by the transfer of photoionization approaches from an academic into an industrial environment. The workshop audience was comprised of 49% attendants working in an academic environment, 36% from industry, and 15% who see themselves in between academia and industry.

Discussion:

- Lively discussion between participants,
 - routine application of APPI;
 - APPI vs ESI: unused potential for mechanistical interpretation of PI spectra;
 - focus on simple APPI implementation, comparable to ESI;
 - strong differences and no comparison of APPI source implementations
 - interest in low pressure PI, its use and deployment
- Several participants used the opportunity to ask application-oriented questions,
 - choice of dopant for APPI of heavily halogenated aromatic molecules;
 - amount of toluene as dopant for unknown molecules from pharmaceutical QC;
 - recommendations for optimization workflow for DA-APPI
- Other general comments included,
 - in industry, you have to solve 'the problem' so APPI is a valuable tool
 - the tool needs to be robust and validated methods are good, but different industries can customise tools for their needs



Universität
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C2MC
Complex Matrices
Molecular Characterization

PHOTOIONIZATION (APPI/PI) - BRIDGING THE GAP BETWEEN ACADEMIC AND INDUSTRIAL RESEARCH

Christopher P. Rüger^{1,2,3}, Johann Le Maître^{1,3,4}, Marie Hubert-Roux¹,
Benoit Paupy⁴, Sabrina Marceau⁴, Carlos Afonso^{1,3}, Pierre Giusti^{3,4},

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³ International Joint Laboratory - iC2MC: Complex Matrices Molecular Characterization, France

⁴ TOTAL Refining & Chemicals, Total Research & Technology Gonfreville, France

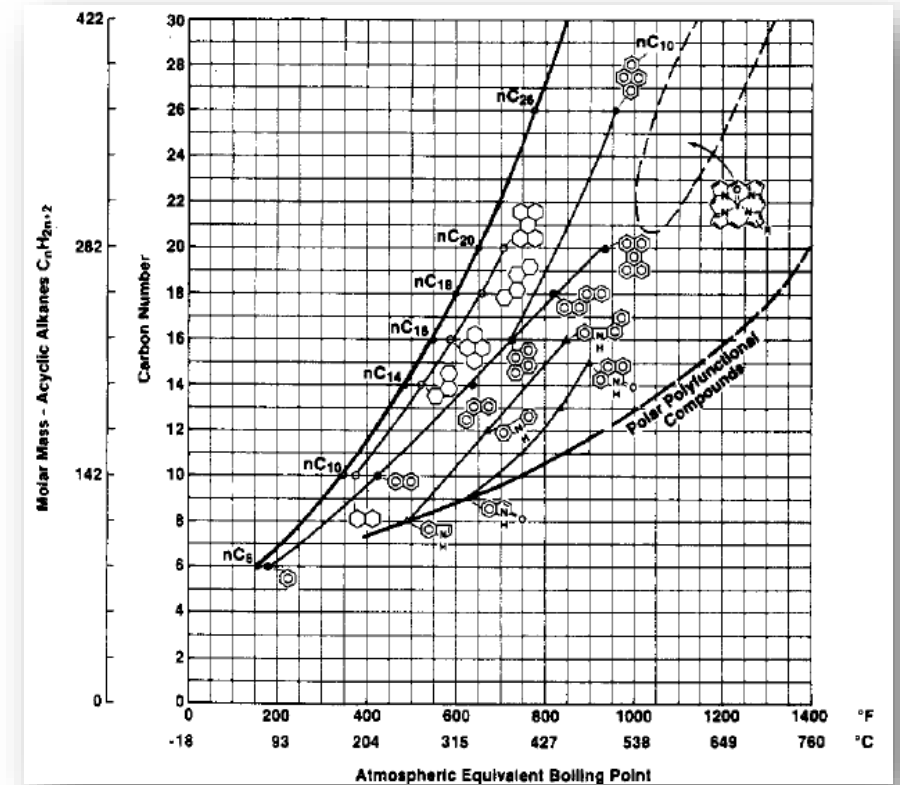
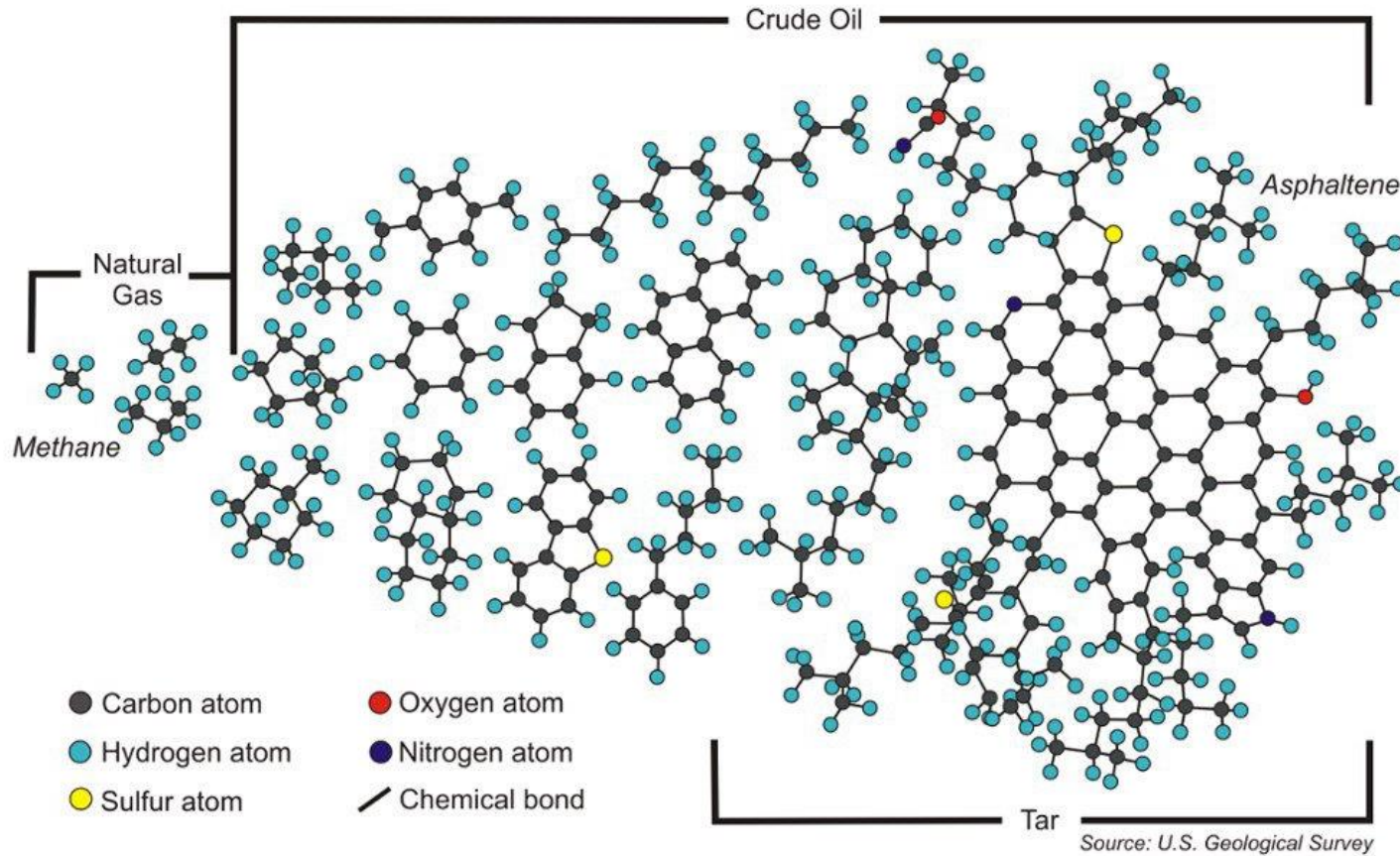


Annual conference of the American Society for Mass Spectrometry
(ASMS), Atlanta (Georgia) - 03.06.2019

OUTLINE

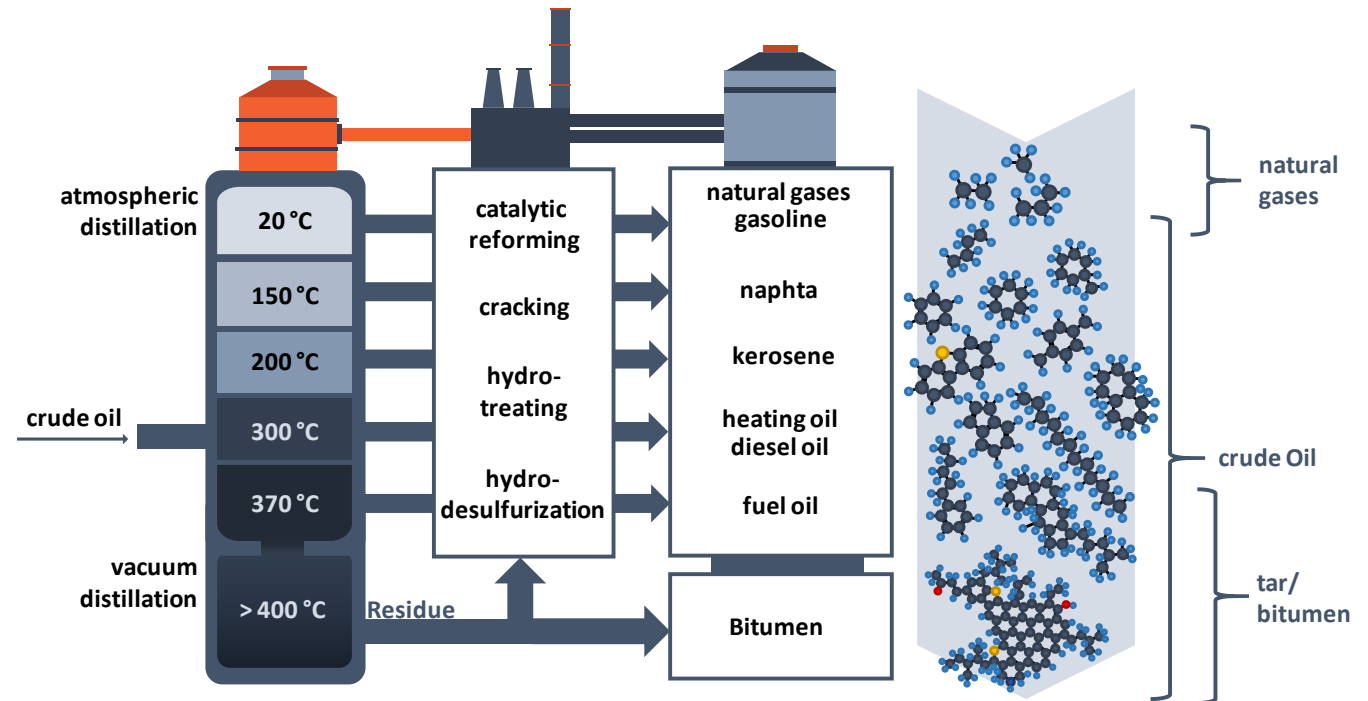
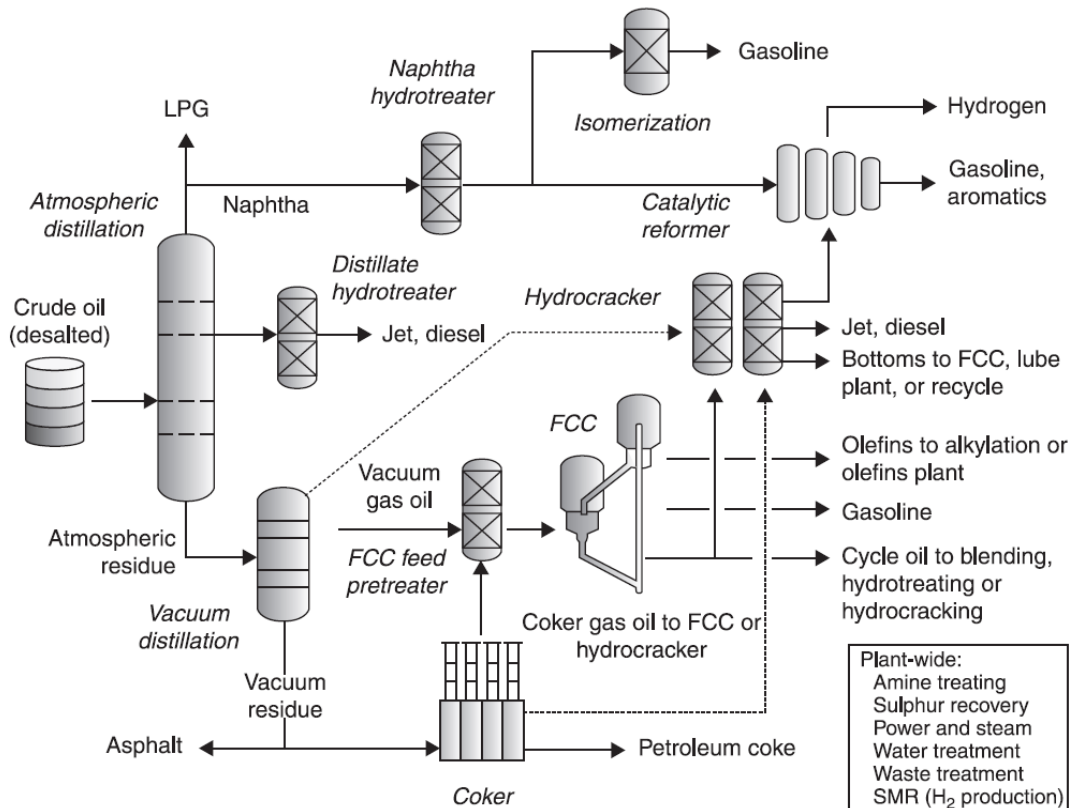
- **Motivation and Application in the Petrochemical Sector**
- **Instrumentation for Photoionization**
- **Application Examples and Current Challenges**
- **Conclusion – Bridging the gap?**
- **Questions and Future Whishes**

MOTIVATION AND APPLICATION CONTEXT: PETROLEUM COMPLEXITY



→ wide range of chemical functionalities, m/z -range from < 100 up to > 1000 , mostly CHNOS and some metals (Ni, V, Fe), tremendous isobaric and isomeric complexity

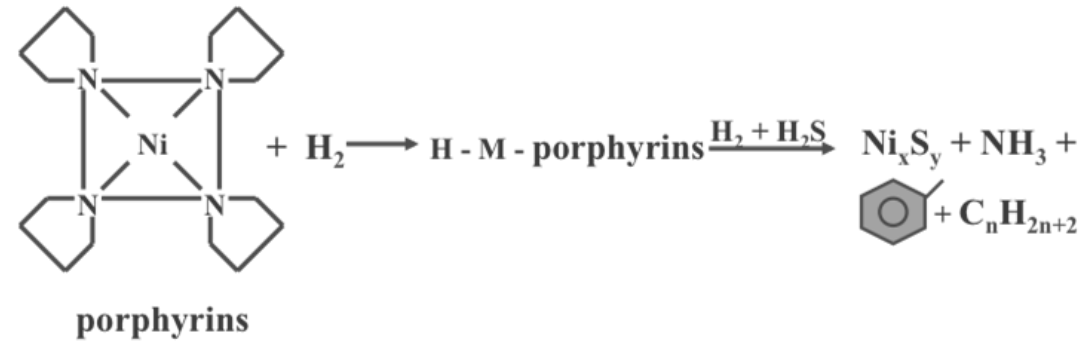
MOTIVATION AND APPLICATION CONTEXT: PETROLEUM COMPLEXITY



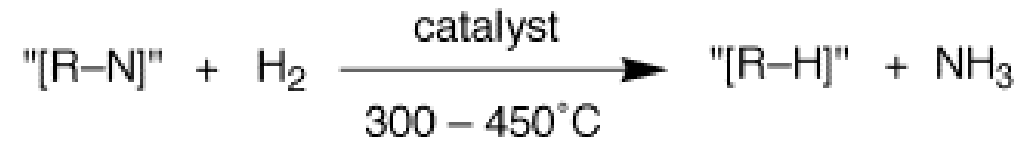
→ wide variety of processes and reaction schemes (distillation, thermal/catalytic conversion, etc.)

MOTIVATION AND APPLICATION CONTEXT: IMPORTANT PROCESSES

- HDM (Hydrodemetalation)



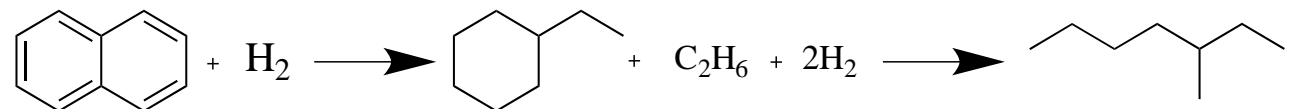
- HDN (Hydrodenitrogenation)



- HDS (Hydrodesulfurization)



- HDC (Hydrocracking)



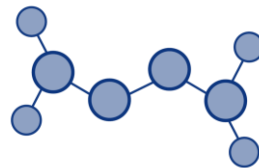
MOTIVATION AND APPLICATION CONTEXT: PETROLEUM AND POLYMERS

Petroleum analysis

- up-stream challenges (feed analysis, enhance-oil-recovery, etc.)
- down-stream challenges
(refining processes: HDM, HDN, HDS, hydro/thermal cracking)
- product and marketing challenges
(final product specification, additives, aging and transport)
- alternative fuels (biofuels, pyrolysis fuels, etc.)

Polymers

- following polymer production process
- final polymer products (films, tablets, powder)
- investigation of chemical composition versus physical property relationships



INSTRUMENTATION – IMS-HRTOF-MS AND FTICR-MS



**BRUKER 12T SOLARIX XR
@ UNIVERSITY OF ROUEN**

- direct infusion ESI, APCI, APPI
- direct inlet probe APCI, APPI
- liquid chromatography
- gas chromatography APCI, APPI




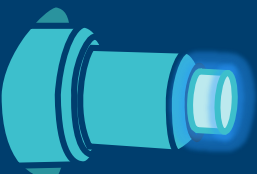
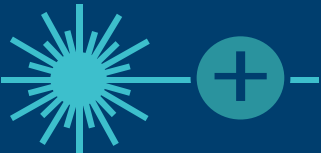

**WATERS SYNAPT G2
@ UNIVERSITY OF ROUEN**

- direct infusion ESI, APCI, APPI
- ASAP APCI
- liquid chromatography
- gas chromatography APCI, APPI

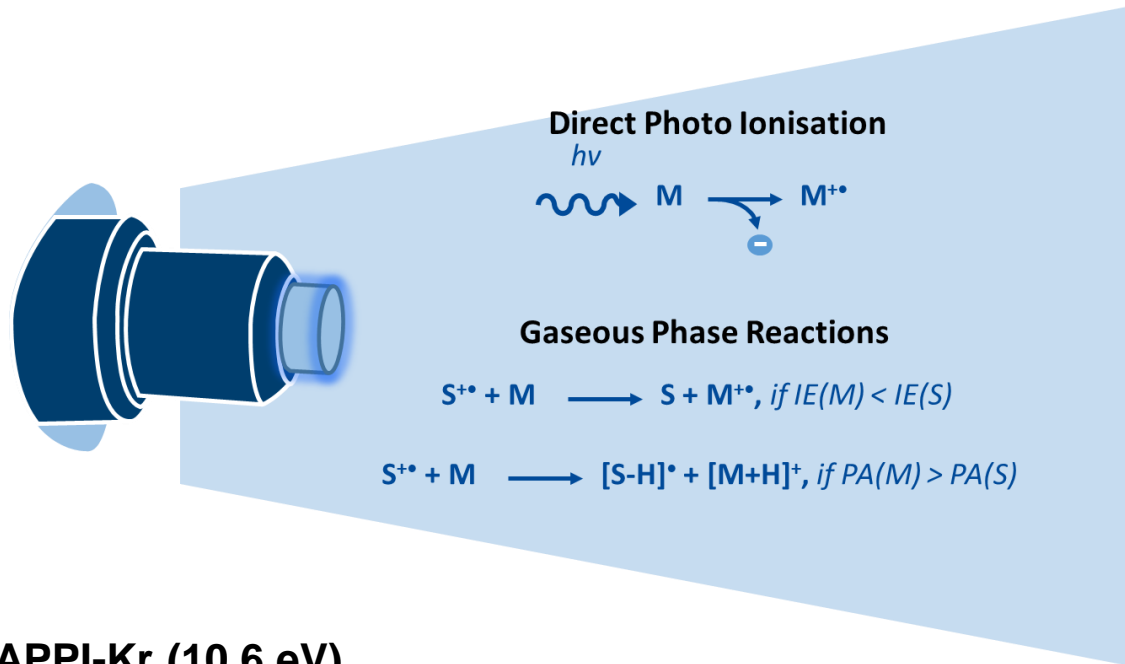


**WATERS SYNAPT G2 SI
@ TOTAL TRTG**

INSTRUMENTATION – ATMOSPHERIC PRESSURE PHOTOIONIZATION

			
APCI	APPI	APLI	ESI
Polar, semipolar compounds (particularly oxygen species)	Semipolar, non-polar compounds (particularly sulfur species)	Polyaromatic hydrocarbons only	Polar compounds
Liquid or gaseous sample introduction	Liquid or gaseous sample introduction	gaseous sample introduction	Direct liquid injection method

INSTRUMENTATION – ATMOSPHERIC PRESSURE PHOTOIONIZATION



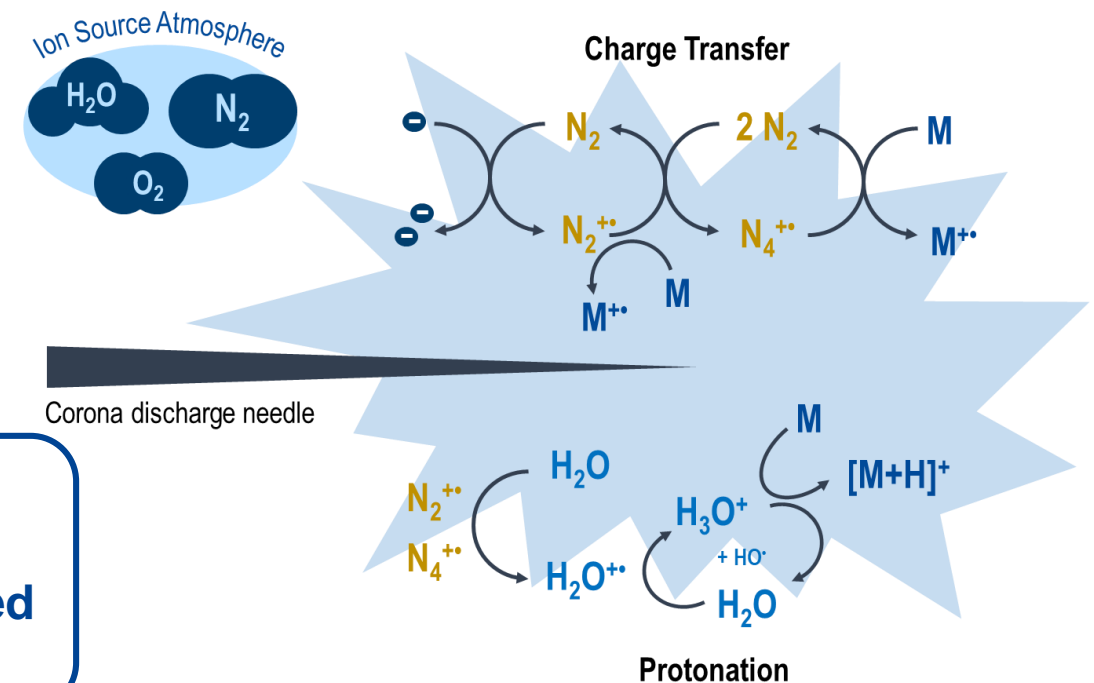
APPI-Kr (10.6 eV)

- broad chemical space
- unpolar species ionised
- radical + protonated ions

Which one to use for which application?
 Bridging the gap by generalized rules and concepts?

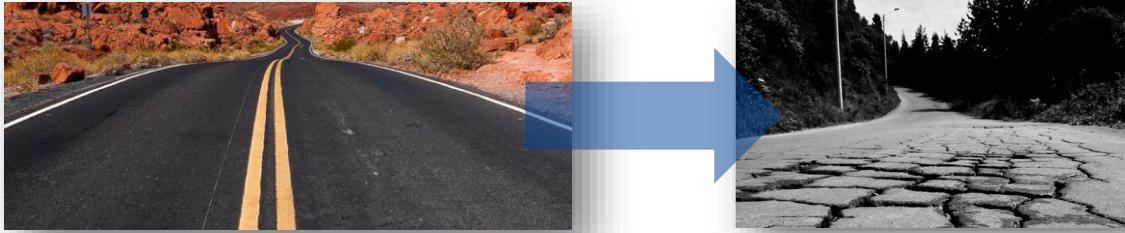
APCI

- for polar compounds
- plasma induced proton/charge transfer reactions
- most often protonation pronounced, but also radical cation formation



APPLICATION EXAMPLES AND CHALLENGES: BITUMEN DIRECT INFUSION

Investigation of Bitumen aging on the molecular level

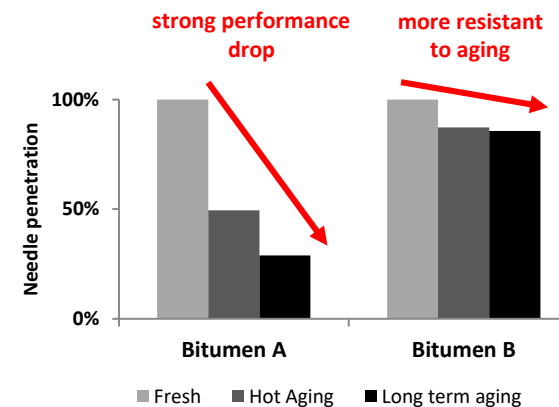


Bitumen is only specified (ASTM D946) by physical parameters:

- penetration grade → hardness and classification
- breaking point → properties at low temperatures
- softening point → properties at high temperatures

but chemical composition determines:

- lifetime and aging
- compatibility with additives
- adhesion to aggregates
- in-service performance



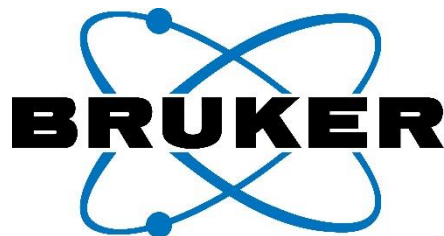
CONCLUSION

- ESI-MS and GC/GCxGC-EI-MS are the routine approaches
- APCI is very rare (usually only in the combination with ASAP)
- photoionization is a “semi-routine” technique in C2MC/Total **but** strongly related to specific applications

- APPI as complementary technique to ESI and for finger-printing
- vast complexity observed with APPI does not directly allow the transfer on the HR-TOF platform and creates new challenges for data processing and interpretation workflows
- in particular deployed for CH/CHS_x-class related aspects (HDS, feedstock description)

- no vacuum photoionization deployed in the industrial context (so far)

ACKNOWLEDGMENT



Complete team of:

International Joint Laboratory Complex Matrices Molecular Characterization- iC2MC

Joint Mass Spectrometry Centre Rostock and Munich - JMSC

Thank you for the attention!
christopher.rueger@uni-rostock.de



QUESTIONS AND FUTURE DEMANDS ON APPI/PI FOR PETROLEUM INDUSTRY

Questions

- Does the progress in laser technologies allows for the application of APLI in routine laboratories in the near future, e.g., distinguishing naphthenic and aromatic constituents more easily?
- Does the sensitivity of photoionization applications, e.g., PI-GC from Jeol, allow tracking trace components, e.g., impurities after refining, additives in final products, etc.?
- Are there any commercial attempts for GC-APPI from the manufactures?
- Can we retain certain selectivity for APPI but lowering the isobaric complexity to allow for an increase usage on the HR-TOF (Synapt) platform?

Request and future demands

- ionization of saturates beyond the GC/GCxGC accessible range
→ lubrication oils, waxes, polymer degradation, etc.
- quantification in atmospheric pressure ionization (APPI)
- general preparation protocols regarding dopants

Pierre Giusti (Total, France): *“(HT) GC-SPI-IM-MS for isomeric description of chromatographically unresolved isomers (especially on saturates) in (heavy) oil fractions”*



Development of a Novel Elemental Analysis Technique for Nuclear Decommissioning based on Colinear Resonance Ionisation Spectroscopy

Giles Edwards

Nuclear Physics Group

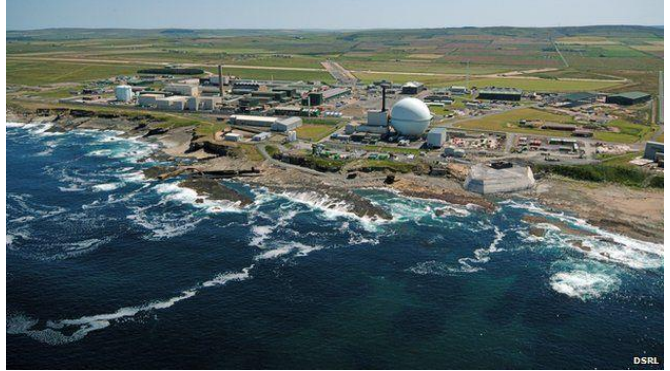
The University of Manchester

Overview

- Nuclear Decommissioning Challenges
 - The problem...
 - Elemental analysis using ICP-MS or ICP-MS/MS ?
- Elemental Analysis using Photoionisation?
 - Single Photon Ionisation
 - Resonance Ionisation Mass Spectrometry (RIMS)
- Colinear Resonance Ionisation Spectroscopy (CRIS)
- Hyperfine Structure
- CRIS at the ISOLDE facility, CERN
- Hypehation of CRIS to ICP-MS (ICP-MS-CRIS)

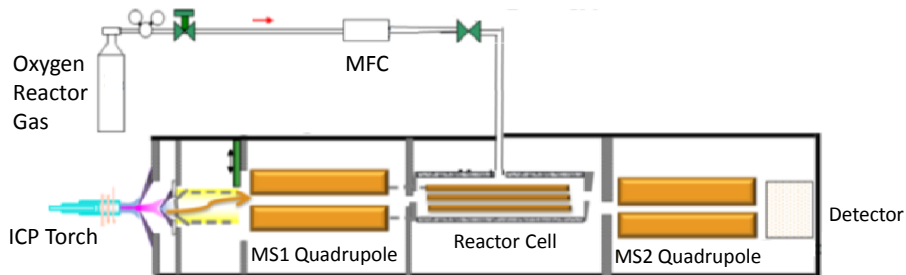
Nuclear Decommissioning - Problems

- Huge legacy of nuclear waste - land requires remediation
- Estimates of between £200 billion to £1 trillion clean up cost in UK alone over the next 200 to 300 years
- Need to characterise & quantify the materials to make a decision on which waste stream for clearance
- Strontium-90 is the most difficult (time consuming) nuclide to quantify at the required lower limit
- Other problem nuclides include, C-14, Fe-55, Kr-85, Mo-93, Nb-93m, Ni-59, Ni-63, Pm-147, Pu-241, Sm-151, Tc-99



Use of ICP-MS or ICP-MS/MS ?

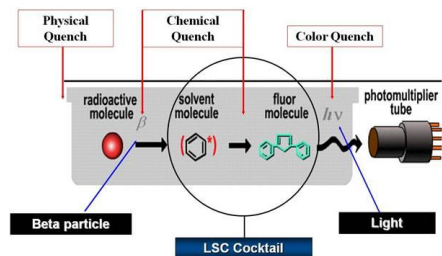
- ICP-MS used for many assays however it is not suitable for strontium-90 due to a large isobaric interference peak for zirconium-90
- ICP-MS/MS has been tried using oxygen in the reactor cell



- The reaction of ^{90}Sr is endothermic whereas ^{90}Zr and ^{90}Y are both exothermic resulting in removal of unwanted matrix interference

Use of ICP-MS/MS ?

- Unfortunately the sensitivity of ICP-MS/MS is not sufficient for the LLOQ required for 'release' of strontium-90 in landfill waste stream
- The only method currently available involves liquid scintillation counters, the ingrowth period of the yttrium-90 decay product that can be isolated via wet chemistry method takes from 20-30 days
- This is a long time for site remediation with soil excavation - have to know when to stop digging...



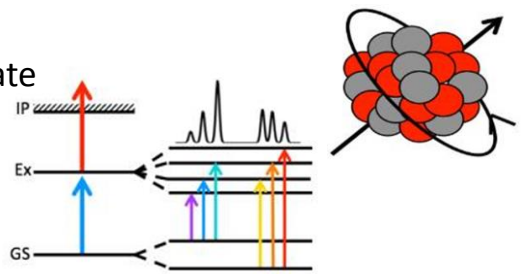
Elemental Analysis using Photoionisation?

- Single Photon Ionisation (SPI)
 - Fluorine excimer laser at 157 nm (7.9 eV) covers ~60% of periodic table but with **no selectivity**
 - Need to rely on the mass analyser for **specificity** (high mass resolving power of ~100,000 to resolve ^{90}Sr from ^{90}Zr)
 - **Abundance sensitivity** this is the contribution of the peak tail to an adjacent m/z value
- Resonance Ionisation Mass Spectrometry (RIMS)
 - High selectivity, increases with number of transitions step
 - Technique often let down by poor mass resolving power/ abundance sensitivity

Colinear Resonance Ionisation Spectroscopy

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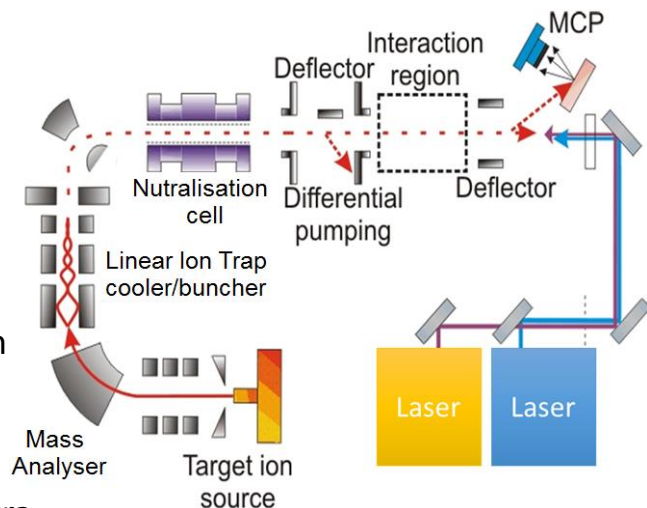
- CRIS of an accelerated atom or ion beam (>10 keV) with very low energy spread enables observation of hyperfine structure (high resolution spectroscopy)
- Possible to deduce magnetic dipole moment, charge radii, angular momentum of nucleus & electric quadrupole moment
- Doppler laser line width reduced due to low energy (velocity) spread of atom beam in ground state
- Laser frequency scanned to generate atomic spectra
- High selectivity enables isotopic resolution of low abundance isotopes (**high abundance sensitivity**) due to Doppler shift



ISOLDE/CRIS Experiment at CERN

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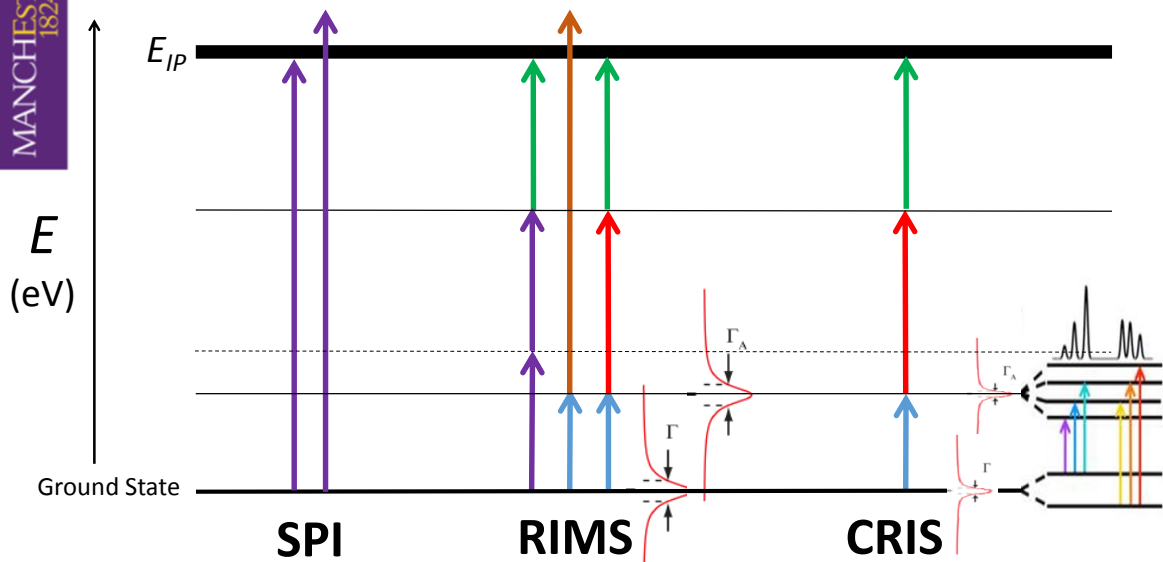
- Exotic nuclei created using 1.4 GeV protons
- Ion beam accelerated to 30-50 keV
- LIT cooler/buncher
- Ion beam neutralised by alkali metal vapor
- Fast atom beam enters colinear resonant ionisation interaction region
- Laser linewidth 15-50 MHz
- Laser frequency scanned to generate hyperfine spectra



ISOLDE/CRIS Experiment at CERN

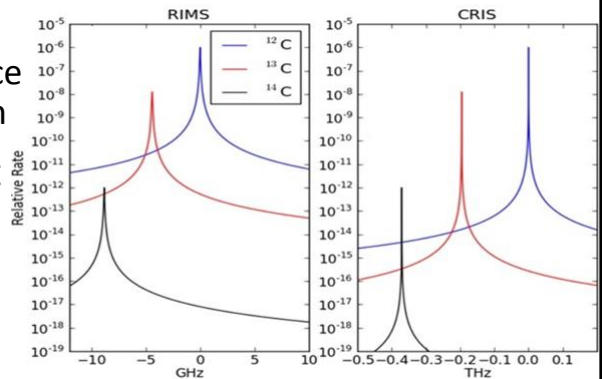
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SPI, RIMS & CRIS

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RIMS vs. CRIS ?

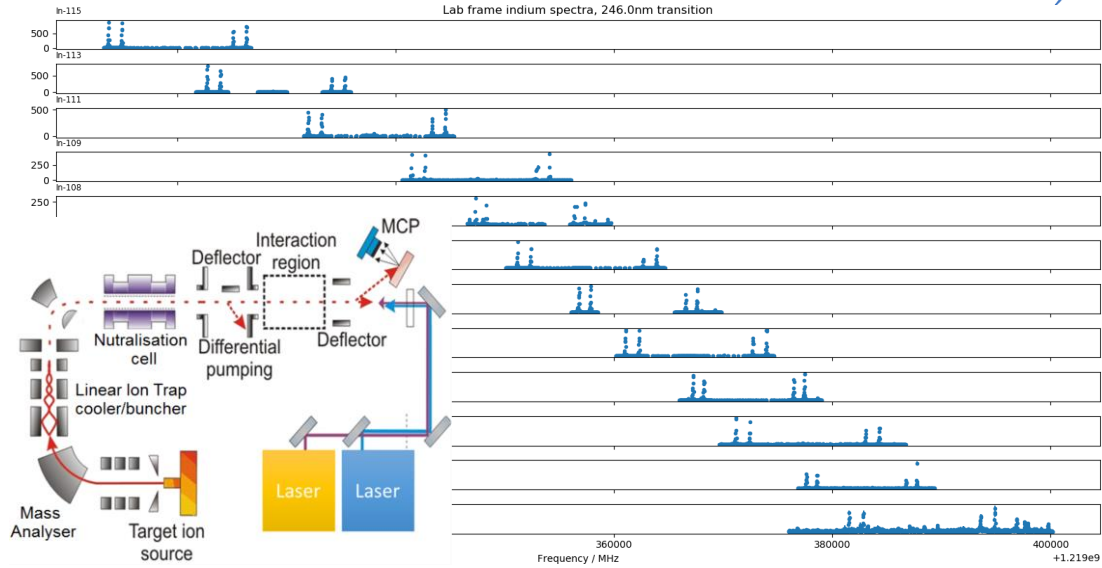
- Simulation is for a single resonance $^1S_0 \rightarrow ^1P_1$ transition at 247.8 nm
- The low relative abundance of ^{14}C is masked by ^{13}C & ^{12}C peak tails
- Need to increase selectivity for RIMS by increasing number of transitions (more lasers)
- Ions ejected from trap in tight bunch to reduce the energy spread (narrower peaks, kinematic compression)
- Peaks further apart due to Doppler shift which increases selectivity analogous to **abundance sensitivity**



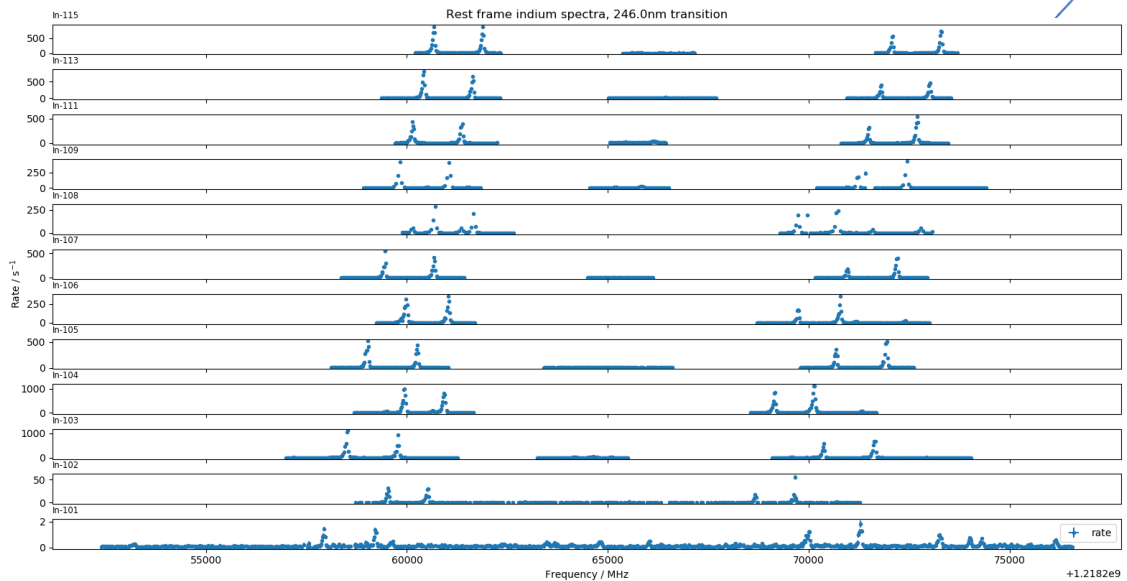
Doppler shift & CRIS?

- Also known as kinematic shift – this is due to laser beam being propagated colinearly with respect to atom beam
- The amount of shift is proportional to the velocity of the atom beam with respect to the laser beam, all ions ejected from trap with the same kinetic energy
- **Isotopic selectivity** based on each **isotopes velocity**
- **Time-of-flight** of ions from trap to laser interaction region gives an additional level of selectivity, timing of laser pulse & trap ejection tuned for each isotope
- **Doppler red shift** = shift in spectrum to **lower frequency** if laser beam propagated in same direction as atom beam
- **Doppler blue shift** = shift in spectrum to **higher frequency** if laser beam propagated in opposite direction of atom beam

ISOLDE/CRIS Experiment - Indium

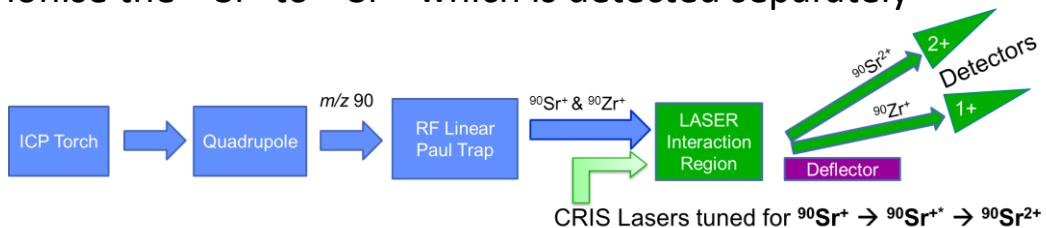


ISOLDE/CRIS Experiment – Indium (Doppler corrected)



ICP-MS-CRIS

- Project running to 'hyphenate' an ICP-MS instrument to our CRIS setup at the University of Manchester
- Perkin Elmer DRC II ICP-MS instrument being 'up cycled' for the project
- No need for neutralisation cell, 1+ ion beam from the quadrupole is bunched & ejected, lasers tuned to resonantly ionise the $^{90}\text{Sr}^+$ to $^{90}\text{Sr}^{2+}$ which is detected separately



Spin-out Company



- The University of Manchester encouraged Dr Kieran Flanagan (Principal Investigator) to setup a spin-out company
- Registered "Artemis Analytical Ltd" in 2016
- Received £10 000 for a 2% state in the company from the University
- Preparing governance documents and setting team (currently three people)
- Have access to Innovate UK funding and VC investment (alternative funding)
- Looking for seed equity investment

www.artemis-analytical.com

Summary

- Use of CRIS combined with ICP-MS allows for rapid quantitation of ^{90}Sr offering a strategic advantage in terms of understanding its mobility, diminution and control within the environment
- ICP-MS-CRIS quantitation can be achieved with the detection limits required with high throughput sample handling
- The universal benefits of CRIS lies in the fact that it can be applied to any element in the periodic table with unrivalled sensitivity & selectivity

K. T. Flanagan *et al.*, Phys. Rev. Lett. **111**, 212501, 2013

R. P. de Groote *et al.*, Phys. Rev. C, **96**, 041302, 2017

Acknowledgements

- Dr Kieran Flanagan (Principal Investigator)
- Cory Binnersley, Chris Ricketts & Sultan Alsufyani (Ph.D Researchers)
- Jack Hancock & Matthew Parker (MPhys Students)
- Dr Ben Cooper (Research Associate)
- Andy Smith (Computer Aided Design)
- Jeremy Andrew (Dounreay Site Restoration Ltd)
- Andy Mcfarlane, Colin Read & others (Technical Staff Fabrication)



Poster Presentation

- Poster **WP468** on Wednesday 10:30 to 14:30

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The University of Manchester
Photon Science Institute

Development of Colinear Resonance Ionisation Spectroscopy (CRIS) for sub-ppt IRMS based Assays Including Radiocarbon Dating

Giles Edwards^{1*}, Ben Cooper¹, Sultan Alsaufyani¹, Cory Binnersley¹, Christopher Ricketts¹, Holly Perrett¹ and Karen Flanagan^{1,2}

¹Nuclear Physics Group, School of Physics & Astronomy, The University of Manchester, United Kingdom
²Photon Science Institute, The University of Manchester, United Kingdom

Hypenation of MS to CRIS

- Resonance Ionisation Mass Spectrometry (RIMS) is a high sensitivity technique that is used to ionise ground state atoms in the rest frame, only atoms with electronic transitions corresponding to the photon energies of the laser used will be ionised with high efficiency.
- The CRIS technique has been developed in more recent years at CRIS as a high sensitivity method for probing exotic atomic nuclei. Unlike IRMS ground state atoms in CRIS are resonantly ionised at high velocity in colinear geometry with respect to the laser pulse.
- Kinematic compression increases spectral resolution & kinematic shift increases isotopic selectivity (abundance sensitivity)

$$\Delta E \approx \frac{1}{2} \frac{v^2}{c^2} E_0$$

Figure 1 (a) Deficient of selectivity in resonance ionisation (b) Hypenation setting

- The high selectivity of CRIS enables isotopic resolution of low abundance isotopes to be studied, possible to deduce magnetic dipole moment, charge radii, angular momentum of nuclei & electric quadrupole moment^{1,2}

Figure 2 (a) RIMS & CRIS at 5 keV ionisation for a single ¹²C 1s transition at 281.5 eV to demonstrate selectivity. (b) Schematic of CRIS laser at CRIS

- Ion beam shaped & focused into 2.5 MHz RF linear Paul trap, ions decelerated & collisionally cooled with helium buffer gas

Figure 3 (a) Electron Cyclotron Resonance (ECR) ion source. (b) ECR source in operation with photo of ionised gas. (c) Charge modulator and helix Paul trap

- Fast switching of longitudinal DC potentials synchronised to laser system used to eject ions from trap for temporal overlap with laser pulse in CRIS laser interaction region, section at 5 keV
- Laser interaction region differentially pumped to reduce non-resonance (collisional induced) activation with a background suppression factor of 10³

(1) M. J. Cooper et al., Phys. Rev. Lett. 111, 23301 (2013)
(2) M. J. Cooper et al., Phys. Rev. C, 86, 064602 (2012)

Carbon Dating – An Analytical Challenge?

- ¹⁴C is a radioactive cosmogenic carbon isotope that has a natural abundance at ppt level with respect to ¹²C in the atmosphere, phytoplankton & respiration of living organisms maintain the same relative isotopic abundance until death
- The half life of ¹⁴C is ~5730 years, the chronological time a living organism no longer participated in active carbon exchange with the environment may therefore be calculated back to ~5700 years or 10 half lives which is the current LLCD for ¹⁴C using AMS
- Various atomic and molecular isotopic sample matrix interferences render all but the most exotic of mass spectrometry techniques inadequate, AMS is currently the method of choice for accurate dating
- Need to count 10,000 ¹⁴C atoms quickly (minutes) to match AMS performance this requires a multi-µA ion beam (10¹¹ to 10¹³ ions/second), dark counts reduced by employing a dual channel system for simultaneous ion & electron detection
- Interference suppression factor of better than 10¹⁰ will reduce ¹⁴C & ¹³C to less than 1 cps

Carbon Dating Instrument (GC-MS-CRIS)

Figure 4: Carbon Dating Instrument (GC-MS-CRIS)

Ultraclean Elemental Analysis (ICP-MS-CRIS)

- Robotic interference from difficult sample matrices reduce the efficacy of a simple ICP-MS for certain analytes
- Complex sample preparation, the use of a reaction cell (ICP-MS/MS) or even the adoption of an alternative analytical technique may be required
- The development of ICP-MS-CRIS allows the rapid quantitation of ¹⁰⁹Ag for nuclear decommissioning. ¹⁰⁹Ag is major isotopic interference but ICP-MS/MS not sensitive enough. Important to understand ¹⁰⁹Ag mobility & dispersion within the environment. Current method takes ~30 days per sample, ICP-MS-CRIS ~30 minutes

Figure 5: Hypenation of ICP-MS to CRIS. CRIS ions used to 'Purify' Ag⁺ from Ag⁺

- The targeted analyte ions in the 1+ charge state are resonantly excited & subsequently ionised to the 2+ charge state, the resulting 2+ ions are deflected to a separate detector than the 1+ non-resonant ions with an additional dimension of selectivity

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