Development of a photoionisation spectrometer for detection of atmospheric $^{85}$Kr

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Abstract. A higher than baseline atmospheric concentration of the radioactive fission product $^{85}$Kr is considered to be the best indicator of clandestine plutonium separation. Additionally, its high volatility makes it suitable for detecting leaks in nuclear waste containers and damaged fuel cladding. A spectrometer for ultra-trace analysis is currently under development and will be optimised for atmospheric monitoring of $^{85}$Kr. This device is based on an adapted form of collinear resonance ionisation spectroscopy, a technique developed at ISOLDE-CERN for performing precision measurements on exotic nuclei. The motivation for this device is explored, along with an overview of progress and future developments.

1. Introduction

$^{85}$Kr is a radioactive noble gas present in the atmosphere. Around 0.09 TBq of the total atmospheric inventory is produced naturally through the interaction of cosmic neutrons and the stable isotopic neighbour $^{84}$Kr [1]. However, an estimated 5500 PBq of atmospheric $^{85}$Kr originates from anthropogenic sources. Most of this is released by nuclear reprocessing facilities in the extraction of plutonium from spent nuclear fuel. $^{85}$Kr is produced in nuclear reactions with a fission yield of 0.3% [2]. Unless the fuel cladding is damaged, the $^{85}$Kr formed in reactors 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. A higher than baseline concentration of $^{85}$Kr in the environment of a storage facility can indicate a leak in the fuel containers, as it will escape through any cracks in the cladding due to its high volatility.

During the dissolution of spent fuel for reprocessing, the $^{85}$Kr in the rods is released into the atmosphere, leading to a spike in local atmospheric concentration. If detected, this spike can be used as a signal that a nuclear facility is operating in the vicinity of the measurement. Detection of illegal reprocessing facilities is challenging and cannot be done with satellite imaging, as the buildings used are indistinguishable from other industrial facilities. Because of this, the International Atomic Energy Agency (IAEA) has introduced environmental sampling to the Nuclear Proliferation Treaty (NPT) safeguards [3]. A study published by the IAEA [4] concluded that atmospheric monitoring for radioactive tracers is more likely to be successful than analysis of soil and groundwater, due to large uncertainties and low quantities of the isotopes involved in these measurements. Of the gaseous fission products, $^{85}$Kr is the most suitable for use as
A radioactive tracer. However, its 10.76 year half-life has resulted in a worldwide atmospheric background that would render releases from a facility undetectable at distances of more than a few hundred kilometres [5]. For this reason, random air sampling with a mobile detector system is preferable over a network of fixed monitoring stations, which would incur a high cost. Considering the current background in the Northern hemisphere, at least 50 samples per day would be required to monitor a region of 10 million km$^2$ for the absence of reprocessing activities of more than 270 g Pu per day [4]. Therefore, a $^{85}$Kr monitoring system needs to have high throughput, fast turnaround for sample analysis and a compact design.

$^{85}$Kr is present in the atmosphere with an isotopic abundance of $10^{-12}$ and atmospheric concentration of $10^{-18}$ atm. Because of this, a $^{85}$Kr detector needs high sensitivity and mass resolution to be able to measure the $^{85}$Kr signal over the much larger $^{84}$Kr component, as well as distinguishing it from any isobaric contamination. The most effective technique currently available for $^{85}$Kr measurement is Atom Trap Trace Analysis (ATTA) which selectively traps isotopes in a magneto-optical trap using a resonant laser beam and detects individual atoms through their fluorescence. ATTA is capable of analysing trace noble gases with sub ppt ($10^{-12}$) isotopic abundances [14]. To perform an ATTA measurement, at least 2 $\mu$l of pure krypton gas is separated from an air sample [12]. Including the time taken for this separation process, ATTA can determine the concentration of $^{85}$Kr present in a sample in about 5 hours. ATTA instruments are used exclusively for measurements of isotopic abundances on noble gases.

2. Collinear Resonance Ionisation Spectroscopy

Collinear Resonance Ionisation Spectroscopy (CRIS) is a laser spectroscopy technique developed at the ISOLDE (Isotope Separator On-Line DEvice) facility at CERN for performing high precision measurements on exotic nuclei [22]. During a typical CRIS experiment, an ion beam is neutralised with sodium or potassium vapour and overlapped collinearly with a pulsed laser beam. The laser is tuned to the precise frequency required to excite an electronic transition in the element under investigation. The excited atoms are then ionised using a second laser beam or an electric field. The resulting ions are then electrostatically guided to a charged particle detector for counting [13]. At CERN, CRIS is used to measure the hyperfine structure of atoms in order to extract relative charge radii and magnetic moments. Due to the high selectivity, sensitivity and resolution of the technique, CRIS is also well suited to ultratrace element analysis, in which atoms of an element that make up less 0.0001% of a sample by weight are counted. When modest accelerating voltages are required (5 to 30 keV), as is the case for this project, CRIS can be implemented as a compact, benchtop device which will be adapted to be part of a mobile detector system.

A key problem in trace isotope analysis is eliminating background due to isobars and neighbouring masses. Through maintaining a vacuum in the ionisation region of $10^{-10}$ - $10^{-9}$ mbar, background due to collisional ionisation is minimised [6]. In conventional resonant ionisation mass spectroscopy (RIMS) methods, selectivity is achieved through mass separating the beam within the ion source and magnet, suppressing the signal from neighbouring masses by as much as $10^8$ [16]. However, when measuring extremely rare isotopes with abundant neighbours, such as $^{85}$Kr, the desired signal is drowned out by the tail of the signal from the abundant neighbour. The collinear aspect of the CRIS method introduces improved resolution and additional suppression of neighbouring isotopes. Atoms of all isotopes in a sample are initially ionised and accelerated to a common energy of $qV$, where $q$ is the charge on the accelerated ion and $V$ is the accelerating potential, resulting in a reduction in the Doppler linewidth of the transition. Due to their differing masses, ions of different isotopes move with different velocities, experiencing different Doppler shifts of their transition energies. This introduces an additional kinematic shift between isotopes, $\Delta \nu$, given by
\[ \Delta \nu = \pm \frac{\nu_0 \sqrt{2qV}}{c} \left( \frac{1}{\sqrt{m_1}} - \frac{1}{\sqrt{m_2}} \right) \]  

(1)

where \( \nu_0 \) is the rest-frame atomic transition frequency and \( m_1 \) and \( m_2 \) are masses of neighbouring isotopes. The plus and minus signs correspond to shifts induced when the ion beam propagates collinearly and anti-collinearly with the laser beam respectively [19]. By increasing the separation between neighbouring isotopic peaks, the selectivity of the technique is increased. For example, the natural isotope shift between neighbouring isotopes \( ^{85}\text{Kr} \) and \( ^{84}\text{Kr} \) for the \( 5s^2[3/2]_0 \rightarrow 5p^2[3/2]_2 \) transition is \( 43.4 \pm 6.3 \text{ MHz} \) [20]. When accelerating to 5 keV, the kinematic shift induced is 1.1 GHz. With a natural linewidth \( 2\Gamma \) of 4.4 MHz, the selectivity of this transition is \( 7 \times 10^4 \). As selectivities are multiplicative, using the CRIS method with a two or three step resonant scheme can result in a total selectivity of more than \( 10^8 \). A single CRIS spectrometer is capable of performing selective measurements on elements across the periodic table by adjusting the frequency of the lasers to the relevant transitions and optimising the potentials guiding ions to the detector. This allows for a trace analysis instrument with multi-element capability, which will be optimised for measurement of \( ^{85}\text{Kr} \) as well as other radioactive tracers such as \( ^{14}\text{C} \) and \( ^{90}\text{Sr} \). As part of this optimisation process, a krypton resonance ionisation scheme will be developed. Simulations based on electron-capture cross section calculations [11] have demonstrated that after neutralisation by sodium vapour through the charge exchange process, the metastable \( 5s^2[3/2]_0 \) state in krypton will be 63% populated. Metastable atoms will be resonantly excited to high-lying Rydberg states through an infrared transition, from which they will be ionised with a strong electric field. The overall efficiency of the CRIS technique using field ionisation with a 5 keV beam energy is estimated to be 20%. The estimated efficiencies of each step is given in Table 1. These values are based on measurements from previous experiments and simulations [11][21].

| Process                              | Efficiency |
|--------------------------------------|------------|
| Transmission from ion source to trap | > 90%      |
| Transmission through trap            | 64%        |
| Neutralisation at 5 kV               | 63%        |
| Field ionisation from Rydberg states | 80%        |
| Detection efficiency                 | 80%        |
| Transmission from trap to MCP        | > 90%      |

### 3. Project outline

A CRIS spectrometer is under development at The University of Manchester, for ultratrace analysis of samples containing rare radioactive isotopes. This device will be optimised for the measurement of \( ^{85}\text{Kr}/\text{Kr} \) isotopic ratios. A permanent magnet electron cyclotron resonance (ECR) ion source will be used for the production of krypton ions from atmospheric samples. A radiofrequency quadrupole (RFQ) ion trap is under development to improve the properties of the beam for higher-quality measurements and increased duty cycle, and a field ionisation unit will be installed for the ionisation step. The experimental set-up for \( ^{85}\text{Kr}/\text{Kr} \) measurement is shown in Figure 1.
3.1. Ion production

A permanent magnet ECR source with a continuously flowing gas feed and a maximum magnetic field of 875 Gauss has been developed and is under testing, based on those designed and constructed at Peking University [15]. The ECR source consists of a volume containing electrons and an applied magnetic field, into which 2.45 GHz microwaves are injected. A sample gas is also injected into the volume. When the frequency of the microwaves matches the gyration period of the electrons, the electrons gain enough kinetic energy to ionise the surrounding gas, creating a plasma. The plasma is extracted using electrostatic plates held at high voltage. It has been shown [7] that intense ion beams of up to 50 mA can be produced from air with compact ECR sources. This is beneficial for a CRIS spectrometer, which requires a high throughput to analyse enough air for reliable $^{85}$Kr measurement in as short a time as possible. The CRIS ECR source can continuously and directly sample the air at a flow rate of 1 ml per minute, without the need for sample preparation. This flow rate corresponds to a krypton gas intake of 1 nl per minute. Taking the CRIS efficiency as 20%, as outlined in Table 1, and a $^{85}$Kr isotopic abundance of $10^{-12}$, this results in the detection of 53 $^{85}$Kr atoms in 10 minutes of sampling from 10 nl of krypton gas in 10 ml of air. Therefore, to achieve a 10% statistical uncertainty with a 50 mA beam, the atmosphere would need to be sampled for under 20 minutes. The ECR source will be used in conjunction with a dipole magnet to initially separate $^{85}$Kr$^+$ ions from the primary beam. The $^{84}$Kr$^+$ component will be monitored on a Faraday cup. The rest of the beam, primarily consisting of nitrogen and oxygen, will be dumped onto another Faraday cup. As the light mass beam will be up to 250 W, this beam dump will be cooled with water.

3.2. Radiofrequency quadrupole (RFQ) ion trap

RFQ traps are used at radioactive beam facilities to improve the properties of ion beams for better efficiency, reduced background and higher quality of measurement, by trapping the ions between 4 cylindrical or hyperbolic electrode rods. Applying an RF potential that is 180° out of phase on adjacent rods generates a 2-d RF field with a minimum at the beam axis, confining the ions radially to the centre. The trapping volume is filled with a buffer gas which cools the beam as ions collide with gas particles. The combined effect of cooling and axial confinement decreases the emittance of the ion beam, leading to better transmission through the beamline and a greater probability of interaction with lasers [8]. Additionally, cooling minimises the energy spread of the beam and reduces Doppler broadening of spectral lines, improving the resolution of the technique. A prototype RFQ trap has been developed and is currently under testing with a liquid metal ion source. In the interest of designing a compact, table-top spectrometer, the
RFQ trap has been built using a trapping region of 20 cm. The trap is filled with a helium buffer gas at between $10^{-2}$ - $10^{-1}$ mbar. The DC potential is applied to copper pads set in 3-d printed circuit boards, slotted in between the quadrupole rods. Both rods and DC elements are mounted on polylactic acid (PLA) 3-d printed end caps. The use of 3-d printed materials allows for rapid prototyping and design changes [9], and have been shown to be vacuum compatible in previous work [10]. Ions are injected and extracted from the trap using a series of circular electrodes.

Particle tracing simulations carried out using the COMSOL Multiphysics simulation platform have suggested that the current prototype RFQ trap will be capable of cooling and transmitting a beam of $^{85}$Kr$^+$ with the desirable efficiencies. Collisions of ions with a helium buffer gas were modelled elastically. By performing parametric sweeps, optimal values of the potentials applied to injection and extraction electrodes have been calculated for maximal transmission through the trap. These values are displayed in Figure 2. The transmission efficiency of the injection optics is 94%. Primary losses in beam current occur during the initial extraction phase. The optimal average pressure of the buffer gas in the trapping volume was found to be 0.04 mbar. The prototype trap is currently under testing with a RF frequency of 0.75 MHz. Combinations of RF frequencies and amplitudes for a constant $q$ value of 0.6 were tested to determine the extent of the impact of using larger RF amplitudes. In these simulations, an emittance of 35 $\pi$ mm mrad was used, with a beam current of 100 pA and gas pressure 0.04 mbar. The results are displayed in Table 2.

| $f_{RF}$ / MHz | $U_{RF}$ / V | Efficiency | $\varepsilon$ / $\pi$ mm mrad | Efficiency |
|----------------|-------------|------------|-------------------------------|------------|
| 0.75           | 80          | 8%         | 35                            | 34%        |
| 0.9            | 120         | 14%        | 20                            | 56%        |
| 1.0            | 150         | 14%        | 0.8                           | 64%        |
| 1.1            | 180         | 28%        | 0.2                           | 80%        |
| 1.2            | 210         | 34%        |                               |            |
| 1.4            | 290         | 38%        |                               |            |

Table 2. Results 1: Transmission efficiencies for different RF amplitudes and frequencies, for fixed $q = 0.6$. Results 2: Transmission efficiency for different beam emittances.

Permanent magnet ECR ion sources have been shown to provide beams with transverse emittances ($\varepsilon$) of less than 0.2 $\pi$ mm mrad [17]. The ISOLDE beam emittance depends on the combination of target and ion source used, but has been measured to be 35 $\pi$ mm mrad [18]. Both of these values were tested in the simulation with an RF frequency of 1.2 MHz, RF amplitude of 210 V and beam current of 100 pA. Intermediate values were also tested. The resulting transmission efficiencies are displayed in Table 2. The quoted emittances are root-mean-squared values, using the convention that the area of the trace space ellipse $A = \pi \varepsilon \varepsilon$.

3.3. Conclusion and future work
A CRIS spectrometer for ultra-trace analysis of radioactive isotopes is under development. The design of this instrument will be optimised for the measurement of atmospheric $^{85}$Kr concentrations, which has multiple applications in nuclear safety. A compact ECR ion source will be used with a dipole magnet to produce a Kr$^+$ beam from air samples that will be fed continuously into the source at 1 ml per minute. A compact RFQ trap that will cool and bunch the beam is under testing, with simulations suggesting the trap will be able to successfully cool and transmit a beam of $^{85}$Kr with an efficiency of 60 to 80%, depending on the properties of
Figure 2. A COMSOL simulation tracing $^{85}\text{Kr}^+$ ion transport through the RFQ trap. For this simulation, the buffer gas was at 0.04 mbar, $U_{RF}$ at 210 V with a frequency of 1.2 MHz, beam emittance 0.8 $\pi$ mm mrad and beam current 100 pA. Consecutive DC segments differ in potential by 5 V. The colour scale represents the kinetic energy of the ions.

the beam produced by the ECR source. As primary losses occur during the initial extraction phase, redesign of the extraction optics will be considered. Simulations suggested a significant improvement in transmission with larger RF amplitudes, which will be verified experimentally after the initial phase of testing. As the simulations did not account for space charge effects, these will be incorporated into the next phase of simulations. The trap will also be simulated for bunching the beam, which improves the CRIS efficiency by minimizing duty cycle losses. The CRIS method will be used to selectively excite and ionise $^{85}\text{Kr}$ atoms. The high sensitivity and selectivity of the technique, as well as its capacity to produce fast results from a compact set-up, makes this a competitive method for analysis of trace isotopes in environmental samples, with $^{85}\text{Kr}$ atoms expected to be detected to within 10% statistical uncertainty in less than 20 minutes.

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