Introduction: The isotope ratios of Krypton trapped in presolar SiC grains record the physical properties of s-process sites [1], while Kr isotopic measurements of small samples of primitive meteorites allow the irradiation environment of the early solar system to be investigated [2,3]. Extracting the maximum amount of information from such samples, especially those available in limited amounts such as material returned by the Genesis and Stardust missions, requires instrumentation with extremely high sensitivity (detection limit ~1000 atoms). Such an instrument that employs a resonant photoionisation mass spectroscopy method [4] is under development in our laboratory since 2007 [5]. The latest results are discussed.

Experimental procedure: The development of the time-of-flight mass spectrometer (TOF MS) benefits from its prototype ‘RELAX (Refrigerator Enhanced Laser Analyser for Xenon)’ [6] that has successfully been used for determination of isotopic ratios of Xe in various extraterrestrial samples [e.g. 7]. As a result of step-heating or laser probe the atoms are released from sample into a mass spectrometer volume where condensation at the localized cold spot (~75 K) occurs. After desorption of condensate by 1064 nm Q-switched Nd:YAG laser Kr atoms are ionized by a resonant photoionization laser system and detected by electron multiplier. For calibration and adjustment purposes the known aliquots of air contained 10^7-10^8 atoms of interest can be used.

The Kr photoionization scheme (Fig. 1) employs resonant excitation from the ground state by 116.5 nm vuv light that is generated using four-wave non-linear mixing in Xe (described in details below). The second resonant step employs ~1 mJ/mm^2 at 558.1 nm from a dye laser (Sirah, Cobra) pumped by the second harmonic (532 nm) of a pulsed Nd:YAG laser (Continuum, Powerlight 9010, 10 Hz, ~5 ns pulse width). Part of the fundamental 1064 nm light from the same Nd:YAG laser (~2 mJ/mm^2) is used for the ionization step. We estimate that the ionization region is ~1 mm from the cold spot. All dye lasers are pumped by the same Nd:YAG laser system, beam delay lines being employed to ensure temporal overlap.

VUV generation by four-wave mixing in Xe: Our experimental architecture is adapted from that reported by Thonnard et al. [8]. The Xe levels used for 116.5 nm light generation are shown in Fig.1. The interaction of four coherent optical fields through the third order non-linear susceptibility known as four-wave mixing is well studied [9]. Because of energy and momentum conservation laws, radiation of frequency \( \omega_4=\omega_1+\omega_2+\omega_3 \) is generated if the phase matching condition \( \Delta k_1-k_2-k_3=0 \) is met (\( k \) are wave vectors that depends on refractive index). To meet this condition a xenon-argon mixture can be used as a nonlinear medium. Xenon is negatively and argon positively dispersive in the spectral region near 116.5 nm, so by changing the partial pressures of gases to match the input laser frequencies an optimum condition for vuv light generation at the desired wavelength can be found. The intensity of generated light is given by

\[
I(w_4+w_1+w_2) = N^2|\chi|F(w_4)I(w_1)I(w_2)w_4,
\]

were \( I(w_j) \) is the intensity of the laser light at frequency \( w_j \), \( N \) is the concentration of atoms used in the mixing process, \( \chi \) is the third order susceptibility and \( F \) is a function having maximum when the gas media is phase matched.

In our experiment two collinear 252.6 nm (~1.5 mJ/mm^2) and 1507.3 nm (~1.5 mJ/mm^2) beams pass through the mixing cell (a stainless steel tube 19X180 mm filled with Xe-Ar mixture) that is attached to the ion source of mass-spectrometer via magnesium fluoride viewport. From the other side there are two cells also divided by magnesium fluoride viewport that works as proportional counters.

Fig. 1: Kr photoionization scheme and Xe levels used for four-wave mixing.
Torr of Kr for off-line spectroscopic measurements; another cell contains ~ 10 Torr of nitric oxide (NO) that is easily ionized by vuv and thus used for vuv generation monitoring.

The dependence of optimum Ar/Xe ratio on output vuv wavelength at constant Xe pressure is shown in Fig. 2. The Xe partial pressure was set to 60 Torr and small amounts of Ar were added into the gas mixture. At each new Ar/Xe ratio, the IR laser was tuned until the VUV signal measured in the NO cell was maximized. Peak generation shifts towards longer wavelengths as the Ar/Xe ratio increase; as the partial pressure of argon increases, contributing positive dispersion, the phase mismatch introduced into the system can be compensated for by shifting towards longer wavelengths where the refractive index of xenon is smaller.

The optimal ratio of partial pressures obtained within our experiments is $P_{Ar}/P_{Xe}=9.2$ ($P_{Xe}=60$ Torr; $P_{Ar}=550$ Torr) (Fig.2). At this value the intensity of generated 116.5 nm light is at maximum and the first Kr transition is saturated. The fine tuning of the first transition can be achieved by changing the wavelength of the IR laser beam.

Ultra trace amounts of Krypton detection: The easiest way to probe the developed method for the first time was to use an air as the isotopic ratios are precisely known. A noncumulate eucrite Stannern was used as a reference extraterrestrial material.

Having optimized the experimental conditions we observed stable generation of VUV beam. The green and IR beams were aligned into the ion source to complete the ionization process. The cold finger was operated at 75 K. The VUV power density was estimated <1 $\mu$J/mm$^2$. The power densities used for the second and the third ionization steps were 1 mJ/mm$^2$ and 2 mJ/mm$^2$ respectively.

Aliquots of air containing 10$^6$ atoms of krypton were gettered to remove active gases and then introduced into the mass spectrometer and the time-of-flight signal recorded.


Fig. 2: Experimental argon-xenon ratios of phase matched gas mixture for the wavelengths in the vicinity of the first Kr transition used in excitation scheme. The xenon partial pressure was kept constant 60 Torr.

Fig. 3: TOF spectra of Krypton measured for air samples and Stannern meteorite. In both cases the total Kr content was 10$^6$ atoms. In the air spectrum the $^{84}$Kr peak corresponds to 5.7x10$^5$ atoms and $^{80}$Kr peak to 2.3x10$^5$ atoms.