CHARACTERISTICS AND APPLICATIONS OF RELAX, AN ULTRASENSITIVE, RESONANCE IONIZATION MASS SPECTROMETER FOR XENON. S. A. Crowther, R. K. Mohapatra, G. Turner, D. J. Blagburn, J. D. Gilmour, *SEAES, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. (sarah.crowther@manchester.ac.uk)*.

RELAX [1] - **R**efrigeration **E**nhanced **L**aser **A**nalyser for **X**enon - combines a number of features to achieve the most sensitive instrument for determination of xenon isotope ratios currently available. It consists of a resonant ionization ion source, a cryogenic sample concentrator and a time of flight mass analyser.

The resonant ionization ion source uses a pulsed, ultraviolet laser to excite then ionize xenon atoms. It adopts the excitation / ionization scheme of Chen *et al* [2]. The laser is tuned to exactly half the energy required for the transition between the ^1S ground state and the $^2P_{3/2}6p[1/2]_0$ (j_1l coupling) excited state of xenon, 249.6 nm. Two photons at 249.6 nm are used for excitation, followed by a third photon of the same wavelength for ionization. Using a resonant ionization scheme means that xenon is the only atomic species to be ionized. Within the volume of gas illuminated by the laser beam this ionization process is very efficient.

Gas in the instrument is condensed onto a cold spot produced by the cryogenic sample concentrator which adopts the principles of Hurst *et al.* [3] and Thonnard *et al.* [4]. The gas is then released again by a pulse from a heating laser. The ionization laser fires through the plume of released gas while the sample is concentrated in the ionization volume. The xenon ions are then detected by a time of flight mass analyser. This protocol is well matched to the pulsed ion source since it allows the detection of all the xenon isotopes produced by a laser pulse.

Figure 1 shows a mass spectrum of xenon derived from the Earth's atmosphere. The inset shows the ^{124}Xe and ^{126}Xe

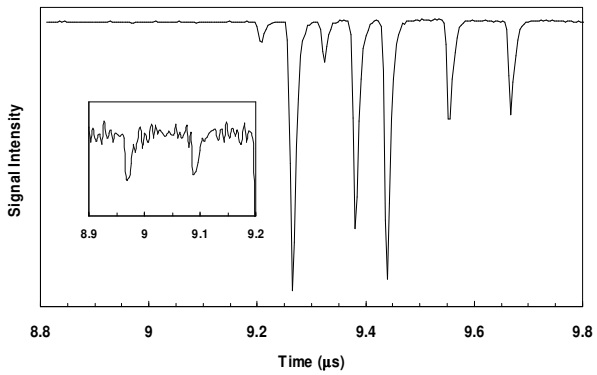

Figure 1: A typical time of flight mass spectrum in the xenon region, produced by summing the mass spectra produced by 100 individual pulses over a time period of 10 s, from a sample of gas containing 7.4×10^5 atoms of ^{132}Xe.

peaks which are not clearly visible on the larger scale of the main spectrum. This spectrum was produced by a sample of air containing typically 7.4×10^5 atoms of ^{132}Xe, which corresponds to 2.8×10^{-14} cc STP of ^{132}Xe.

RELAX calibration aliquots are produced from a reservoir of atmospheric xenon calibrated in turn against the Manchester VG5400 instrument. Aliquots from this reservoir (2.3×10^{-11} cc STP ^{132}Xe) are expanded into a secondary volume, which is in turn sampled yielding a RELAX calibration sample of 1.2×10^5 atoms of ^{132}Xe (4.4×10^{-15} cc STP ^{132}Xe). Sample and secondary standard gas quantities can be determined from the calibration aliquot either by comparison of signal intensities or by making use of a monoisotopic ^{128}Xe spike.

The sensitivity of RELAX depends greatly on a number of parameters such as the operating temperature and the delay between firing the heating and ionising lasers. Figure 2 illustrates the effect different delay times have on the intensity of the initial observed signal and the observed pumpout speed of the xenon. The optimum delay between firing the heating

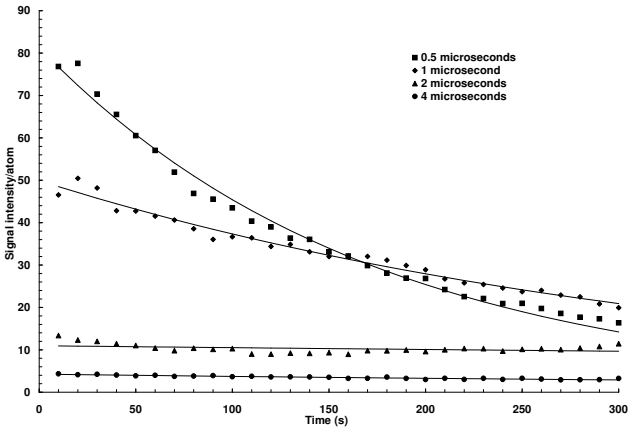

Figure 2: Signal intensity against time, to show the dependence of the signal and pumpout curve on the delay between firing the heating and ionising lasers.

laser and the ionising laser has been found to be around 0.5 μs. If the delay is shorter than 0.5 μs the xenon released from the cold spot has not had time to reach the ionization region when the ionising laser is fired; if the delay is longer than 0.5 μs the gas has travelled beyond the ionization region by the time the second laser is fired. The lifetime against ionization is given by $\tau_{\frac{1}{2}}$:

$$\frac{dN}{dt} = -kN \quad (1)$$

where

$$k = \frac{\ln 2}{\tau_{\frac{1}{2}}} \quad (2)$$

For the optimum delay time of 0.5 μs the sample has a lifetime against ionization of $\sim$ 120 s. Varying the delay decreases the

ionization efficiency, which in turn results in a drop in signal intensity and an increase in the lifetime against ionization.

The importance of the delay time between the two lasers is further illustrated by Figure 3. The left-hand graph in Figure 3 simply shows the initial signal intensities against the delay time, for the same four delay times illustrated in Figure 2. From Figure 2 we can calculate the half life of the signal at the different delay times examined, and initial signal intensity is then plotted again the inverse of these half lives in the righthand graph of Figure 3.

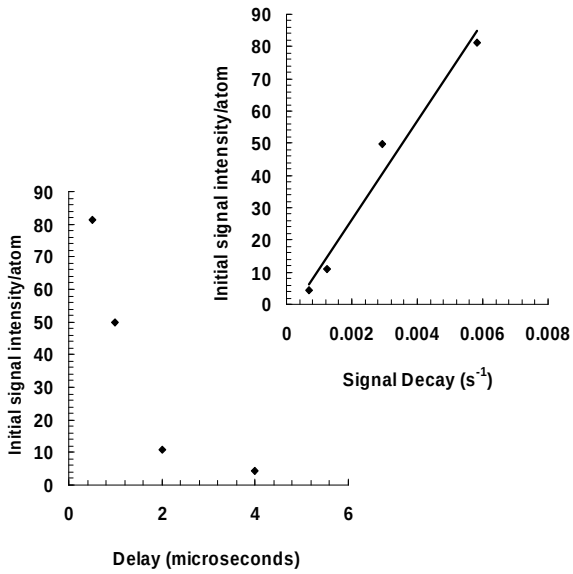

Figure 3: Initial signal intensity against delay time and 1/delay to illustrate the effect of changing the delay between firing the two lasers.

Similar plots can be drawn to illustrate the effect the temperature of the cold spot has on the initial signal intensity and the pumpout speed of the xenon. Tests have shown that the optimum temperature for operation is around 80 K. The operating temperature has been chosen to prevent condensation of the sample onto the cold spot - at this temperature xenon gas is trapped on the cold spot and readily re-released by the heating laser. There is a linear relationship between the ionization signal from a known amount of gas and the pumping speed in Figure 3. This demonstrates that ionization pumping, rather than condensation onto unilluminated regions of the cold spot, is the dominant process removing gas from the mass spectrometer. At colder temperatures more xenon is trapped on the cold spot than can be released by the heating laser and condensation onto unilluminated regions becomes the dominant process of removing gas; at higher temperatures not enough xenon is trapped on the cold spot.

The wide variety of applications of the RELAX mass spectrometer is illustrated by accompanying abstracts - Busfield *et al.*, Busemann *et al.*, Whitby *et al.* and Mohapatra *et al.*.

References [1] Gilmour J.D. *et al.* (1994) *Rev. Sci. Instrum., 65(3)*, 617 - 625. [2] Chen C.H. *et al.* (1980) *Chem. Phys. Lett., 75(3)*, 473 - 477. [3] Hurst G.S *et al.* (1984) *J. Appl. Phys. 55(5)*, 1278 - 1284. [4] Thonnard N *et al*. (1986) *Institute of Physics Conference Series 84*, edited by Hurst G.S. and Morgan C. (Institute of Physics, Bristol).

Acknowledgements This work was funded by the Particle Physics and Astronomy Research Council.