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Photon Burst Mass Spectrometry for the Measurement of ^{85}Kr at Ambient Levels

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ABSTRACT

Photon Burst Mass Spectrometry has been used to measure ^{85}Kr in a sample with an abundance of 6×10^{-9} . Improvements in detection efficiency by the use of avalanche photodiodes cooled to liquid nitrogen temperature are reported, which should make possible measurement of ^{85}Kr at the ambient atmospheric abundance of 10^{-11} .

Keywords: dating, monitoring, abundance measurements, single atom detection, photon burst, mass spectrometry

1. INTRODUCTION

Noble gas radioisotopes are inert chemically and have half-lives ranging from several days to hundreds of thousands of years. Thus they are considered to be ideal probes for dating of geological samples and for various tracer and monitoring applications.¹ The work reported here concerns the isotope ^{85}Kr . It has an atmospheric abundance of 10^{-11} and is a fission product with a half life of 10.7 years. Potential applications include nuclear monitoring, atmospheric transport, and dating young ground water up to 40 years. For ^{85}Kr and other long-lived noble gas isotopes, low elemental concentrations and low isotopic abundance, compounded by low energy decay modes, have made measurement by traditional low level counting methods difficult. Tandem Accelerator Mass Spectrometry, the current technique of choice for ultrasensitive ^{14}C measurements, cannot be used for noble gas isotopes because of the inability to produce a negative ion of these species.

Photon Burst Mass Spectrometry (PBMS) is a laser-based method which has been proposed for ultrasensitive abundance measurements in the 10^{-11} to 10^{-15} range in a variety of elements, including the noble gases.² It combines the high isotopic selectivity of photon burst detection (10^8 demonstrated for Mg^+) with the moderate mass selectivity ($\sim 10^5$) of a mass spectrometer.^{3,4} This technique relies on the detection of a "burst" of spontaneously emitted photons produced by the interaction of a single two-level atom with a resonant laser beam. The photon burst transition used for ^{85}Kr is the $F=13/2$ to $F=15/2$ hyperfine component of the transition between the excited $1s_z$ and $2p_z$ states at 811 nm.

We present in this paper measurements of ^{85}Kr in a commercial sample with an isotopic abundance of 6×10^{-9} .⁵ The primary limitation in this experiment was the low quantum efficiency (QE) of the photomultipliers for 811 nm light ($\sim 3\%$). New large area avalanche photodiodes (APD) cooled to liquid nitrogen temperature are promising replacement detectors.⁶ Test results for ten 5×22 mm APD's are reported here. With the purchase of another dozen APD's, the PBMS instrument should be capable of measuring ^{85}Kr at the ambient atmospheric abundance ($\sim 10^{-11}$).

2. APPARATUS

The layout of the photon burst mass spectrometer is shown schematically in Fig. 1. A Kr ion current of up to 20 μA is generated in a microwave ion source at 40-50 kV potential. It is mass separated in a 126° magnetic sector. Deceleration optics slow the ions transmitted at mass 85 to 2000 eV and focus them into a parallel beam of several millimeters diameter. In a charge exchange cell containing Rb vapor, the Kr^+ ions are converted with high efficiency into metastable Kr atoms.⁷ A tunable diode laser (MicraLase ML-02B) resonantly excites the photon burst transition in the ^{85}Kr atoms. The anti-collinear geometry of the atom and laser beams ensures a long region of overlap and provides reduced Doppler width due to velocity compression in fast beams.⁸ Spontaneous emission from the Kr atoms is collected and counted in ten photon burst detectors with as high efficiency as possible (75% and 3%, respectively), and analyzed for bursts by a series of digital electronic circuits. A gas manifold at the source allows switching and mixing of multiple gas samples, including one with ^{85}Kr at 10 ppm in nitrogen (10^{-2} ^{85}Kr abundance), one with pure Kr at an abundance of 6×10^{-9} , and a third with nitrogen buffer gas.

FIGURE 1. Schematic diagram of the Photon Burst Mass Spectrometry apparatus.

The procedure for the measurement of the 6×10^{-9} isotopic abundance sample was as follows. The PBMS system was first tuned up with approximately equal parts of N_2 and Kr from the 6×10^{-9} sample, and a small amount ($\sim 7\%$) from the high level ^{85}Kr sample. The ^{85}Kr abundance in this mixture was 1.6×10^{-6} , calibrated by comparison of the ^{85}Kr fluorescence count rate and ^{84}Kr current with those of the pure high level sample, in which the ^{85}Kr current was directly measurable. The ^{85}Kr atoms were tuned on and off resonance alternately for 50 seconds each by applying a square wave of 30 V amplitude (equivalent to 650 MHz detuning) to the deceleration voltage. This allowed for subtraction of background signals from stray light and dark counts. After several such cycles, the leak valve to the high level sample was closed off, and the ^{85}Kr abundance in the mixture decayed rapidly to 6×10^{-9} . The fluorescence and burst signals before and after closing the valve were compared to determine the change in the isotope ratio. The ^{84}Kr reference current was constant during this change since the total Kr concentration in the source was only negligibly affected.

RESULTS AND DISCUSSION

Three different measurements of the type described above were made. The raw count rates for total fluorescence on one photomultiplier tube (Tube 9) and for a burst of ≥ 1 photon in 3 of the 9 detectors (Coincidence 3) are shown on the left in Fig. 2 for the first of three such runs (Run K). In resonant periods 1-4 the final tuning of the system with 1.6×10^{-6} abundance was done. The signal levels from periods 4-7 were subtracted from the backgrounds and used for a calibration at 1.6×10^{-6} abundance. The leak valve was closed at the end of period 7, and the ^{85}Kr abundance decayed exponentially to the low level within one 100 second cycle. At 6×10^{-9} abundance on/off resonance cycles were not visible in the raw data due to the background level, but the differences between the on-resonance coincidence 3 rate in one 50 second period and the average the off-resonance rate in the two adjacent periods was observable. The photon burst results (one photon detected in the proper time sequence in three of nine detectors) are plotted in the graph on the right. Fluctuations in individual 100 second

measurements are large, but the average of these six 100 sec measurements, 37(21) bursts/sec (solid line, with the gray area representing the uncertainty) is in reasonable agreement with the expected value, 53 bursts/sec (dotted line).

FIGURE 2. Measurement of ^{85}Kr at 6×10^{-9} abundance: raw data before and after closing the leak valve (left) and difference on-off resonance (right).

The final results for all three measurement runs are summarized in Table 1 both for the photon burst mode and for simple fluorescence in the detector with the best signal-to-noise. All but one of the measured values is within one standard deviation of the expected values for 6×10^{-9} abundance. It is remarkable that measurements of ^{85}Kr at an abundance of 6×10^{-9} were possible to make using the fluorescence recorded in a single detector. A signal of about 50 counts/sec was found in a background of 21,000 counts/second. The high stability of the diode laser and the ion beam is responsible for this success. The background rate in the burst mode (coincidence 3) was somewhat lower (8500 bursts/sec), but the results were not appreciably better. The reason the burst method did not provide a great advantage in this case is that the average total burst size per resonant atom was small (~ 2.2 counts total, or ~ 0.25 count per detector). For comparison, in the Mg^+ measurements, where an abundance selectivity of 10^8 due to the photon burst process alone was demonstrated, the average resonant atom burst size in each of two detectors was ~ 2.8 , or ~ 5.6 counts total. It is apparent that a significant improvement in the quantum efficiency of the detectors at 811 nm over the average photomultiplier (PMT) value of 3.9% would have a huge impact on this experiment. Monte Carlo models of the photon burst process show that the desired goal of ^{85}Kr measurements at the ambient atmospheric abundance (1×10^{-11}) can be reached by increasing the quantum efficiency of the detectors by several times or by reducing the stray light background by an order of magnitude or by some intermediate combination.

TABLE 1. Summary of measurements of ^{85}Kr at 6×10^{-9} abundance

Data run	Integration time(sec)	Coincidence 3 (bursts/sec)		Tube 9 (counts/sec)	
		Measured	Expected	Measured	Expected
K	650	37(21)	53	45(24)	40
L	1000	60(16)	57	88(20)	42
M	950	64(31)	54	60(17)	46

TESTS OF MORE EFFICIENT DETECTORS AT 811 NM

Three candidate replacement detectors with higher quantum efficiency at 811 nm and wide angular acceptance have been tested in our apparatus. These include a hybrid photomultiplier tube (HPMT), an intensified photodiode (IPD) and avalanche photodiodes (APD) from two different companies cooled to liquid nitrogen temperature. All these devices have relatively low gain for single photon pulses (10^3 - 10^4) and hence require the use of slow (~ 1 μ sec) charge-sensitive preamplifiers instead of the fast (nsec) voltage preamplifier which was used with the PMT's.

In the hybrid photomultiplier tube (DEP PPO275B), single photoelectrons from an 18 mm diameter multialkali photocathode are accelerated by a 15 kV potential and focused into a small photodiode. Roughly one extra electron is released in the silicon photodiode for every 3.6 eV of incident electron energy above a threshold of ~ 2000 eV. This results in single photon pulses of ~ 3500 electrons. The main source of spread in the detected pulse heights is preamplifier noise. With this detector and the manufacturer's power supply and preamp, we observed a clear single electron peak. Although the peak was not as narrow as shown in company literature, it was sufficiently isolated so that $\sim 100\%$ detection of photoelectrons was possible. By Rayleigh scattering measurements in our apparatus, we determined the QE of this detector to be 7%. This is close to the 6% value given by the manufacturer. Due to the thick insulation surrounding this detector, putting two HPMT's on an ellipse is not a cost-effective option. Consequently, the HPMT option does not provide a net advantage over the original PMT's since the active diameter (18 mm) is less than half of the length of our elliptical cylinder light collectors (46 mm).

The intensified photodiode (Litton [Intevac] 280AD) is similar to the HPMT except it has a different photocathode (semitransparent GaAs), an lower operating voltage (8 kV), and a small avalanche photodiode in place of the photodiode in the HPMT. The gain of ~ 10 in the avalanche photodiode helped compensate for the low electron impact gain of ~ 1200 at 8 kV. Typical single photon pulses were $\sim 10,000$ electrons. We determined that 80-100% of the single electron pulses could be counted. The specified QE of the GaAs photocathode at 811 nm was $>15\%$. The measured QE at 811 nm, determined by comparison of the Kr atom fluorescence detected in the IPD and in PMT's 2 and 7, was $\sim 10\%$. We do not understand the discrepancy with the manufacturer's specification, although a more limited angular response is a possibility. Unfortunately the avalanche photodiode in the IPD was burned out when an external arc to the high voltage plate of the IPD occurred, so that an independent determination of the QE by Rayleigh scattering was not completed.

High voltage (1400-1800V) avalanche photodiodes, which have sufficient avalanche gain (3000-10,000) for direct single photon counting, are now available commercially. Room temperature photon counting with large area (~ 100 mm²) APD's is not practical because the thermal electron emission rate, $\sim 10^7$ electrons/sec is too high. However, the thermal component of the dark current decreases exponentially with decreased temperature at a factor of 2 every $\sim 8^\circ\text{C}$. Thus at liquid nitrogen temperatures (-196°C), the thermal electron emission rate is <1 electron/sec. With careful design, APD's with very low leakage current have been made, so that counting of single photons with essentially zero dark count rate is now possible. The main limitation in these devices is noise in the preamplifier. This noise is greater in detectors with larger area and hence larger capacitance. Due to the monotonically decreasing pulse height distribution in APD's, a substantial percentage of the amplified single photon pulses are always lost in the preamplifier noise. These detectors also require more care in handling and design of the mounting system because bare semiconductor chips must be used. Others have found that mounted APD's often crack and fail during the thermal cycles.¹¹

We tested two 10 mm diameter APD's from Advanced Photonics and one 13mmx13mm APD from Radiation Monitoring Devices (RMD) in the PBMS apparatus. The characteristics discussed above were confirmed, and a photon counting QE of 20-30% was measured by comparing the photon count rate due to stray light at attenuated laser power with the photocurrent at unity gain and higher laser power. The manufacturer's specified QE at unity gain served to calibrate the input photon flux of stray light. The Advanced Photonics devices had lower average gain (>3000 specified and verified) and somewhat higher unity gain QE (70-80%), and were more robust physically (1 mm thickness). The APD from RMD had higher average gain ($\sim 10,000$ achieved) and moderate unity gain QE (70%), but was extremely fragile. Based on these tests we chose to order a dozen custom 5mmx22mm APD's from RMD. With two such devices mounted on an elliptical collector, an advantage of ~ 3 - $4\times$ in QE over the PMT's is expected.

The twelve custom APD's were mounted in six hollowed out 2.25"x1.6"x1.55" copper blocks. Each APD was held in place between a sapphire window (Edmunds Scientific, some also AR coated) and Teflon pin in which a weak spring was inserted. The spring force was strong enough to hold the devices in place against gravity and mild bumps. The copper blocks were thermally contacted by copper plates and indium contacts to a 5 liter rectangular stainless steel container, which can be filled with liquid nitrogen. The copper plates and blocks could also be heated with plug heaters. The two 0.005" gold contact

wires on each APD were connected to larger wires by silver epoxy rather than solder because there was concern of possible contamination of the semiconductors by solder vapors. After evacuating the detector chamber, the APD's were baked out at -130°C for one hour (a gradual heating and cooling over ~ 8 hours) to remove any water from the surface of the APD's. Cooling the copper blocks to equilibrium at $\sim -170^{\circ}\text{C}$ took about 7 hours. After cooling the devices were run at 1 mA forward current through a 11 k Ω series resistor for a few seconds to break through the silver epoxy contacts. None of our APD's has failed during many heating and cooling cycles over the last year.

Of the dozen devices, two were unusable: one because the leakage current was so high that the operating voltage could not be reached and one because there was no electrical contact. The latter device was one of three in which one gold lead came off during mounting. Repair was attempted with a small dot of silver epoxy but was successful in only two of the three cases. Another device (9A) had a moderately high leakage (10 nA at operating voltage) but was still usable, although at reduced QE due to the noise of the leakage current. The output of each APD was coupled out of the vacuum through a pair of twisted wires and one BNC and one SHV feedthrough. In current measurements, the high voltage was applied through a 1 M Ω resistor (for protection in case of breakdown) to the SHV connector and the BNC connector was routed to a picoammeter. In photon counting mode, the high voltage for each detector was applied through a preamp (eV Products model 5092) with a short cable to the SHV connector, and the BNC connector was shorted to ground. The output of the preamp was amplified by a spectroscopy amplifier (Ortec 472A or Tennelec 205A) with a time constant of 0.25 μsec and a gain of 500. The amplified pulses were fed into a pulse height analysis board in a computer or into a discriminator and counter.

A convenient way to characterize the performance of the APD detectors is to plot the photon counting quantum efficiency, determined by stray light as described above, vs. the background count rate due to electronic noise at each discriminator or minimum pulse height setting. Results for the 10 usable detectors are shown in Fig. 3. These results were obtained by integrating the pulse height distribution recorded in a computer and dividing by the calibrated incident photon flux. Similar data were also obtained point-by-point with the discriminator and counter system. The names 10A and 10B denote the two APD's which are mounted on elliptical light collector number 10. For most of the APD's a QE of 10-25% was obtained at a very low background rate (≤ 3000 counts/sec). Reducing the discriminator level further into the electronic noise generally did not significantly increase the QE, but rapidly raised the background rate. The two exceptions were detector 9A and 9B. In detector 9A the high leakage current limits the performance. The source of noise in detector 9B is not as clear. Specific data at the chosen operating point for each APD are summarized in Table 2. An average counting QE of 15% was obtained at an average background rate of 3200 counts/sec.

FIGURE 3. Photon counting quantum efficiencies for different APD's as determined by integrating the pulse height distributions. Two additional values from discriminator measurements were added for detector 10A. Differences from Table 2 may reflect slightly different applied voltages.

TABLE 2. Photon counting quantum efficiencies at operating voltage and discriminator settings.

APD	Quantum Efficiency	Dark Count Rate
5A	18%	2000
6A	14%	3200
6B	13%	1600
7B	15%	2700
8A	11%	2100
8B	18%	1400
9A	9%	8800
9B	10%	7500
10A	17%	900
10B	25%	1900
Average	15%	3200

The performance of each APD pair for detection of Kr fluorescence was also measured by comparison to that of Tube 2. Results for collectors 6 and 8 are shown in Fig. 4. The APD's are seen to give an improvement of 2.4 and 2.1 over tube 2. Taking into account a 15% loss due to the gap between two APD's on a collector and a poorer angular detection efficiency ($\pm 55^\circ$ vs. $\pm 65^\circ$ FWHM in the PMT's), the predicted improvement factors are 3.0 and 3.3, respectively, based on the measured QE's. A shortfall was also found in the other four APD detectors. The average improvement was 2.1x instead of the expected 2.8x. In trying to understand this repeatable discrepancy, fluorescence data for the 9 PMT's was reviewed and compared to QE's measured by Rayleigh scattering. A linear decrease of 4.8% per detector from detector 1 to detector 10 was found. At present we do not understand this effect. Nevertheless, if a correction is made for this effect, very good agreement is found between the predicted and measured improvement factor for each APD detector (Table 3). The average improvement is then 3.0x, which is close to the predicted 2.8x.

FIGURE 4. Fluorescence spectra of a ^{78}Kr beam at around 2000 eV. The beam energy was scanned slowly, while the fluorescence count rate was recorded simultaneously for two detectors. The FWHM of each spectrum is about 3 eV.

TABLE 3. Measured, corrected and predicted improvement factors for APD detectors compared to photomultiplier 2.

APD position	Measured APD/PMT 2	Corrected APD/PMT 2	Predicted APD/PMT 2
5	1.8	2.2	2.0
6	2.4	3.1	3.0
7	1.6	2.2	1.7
8	2.1	3.2	3.3
9	1.8	2.8	2.2
10	2.6	4.6	4.7
Average	2.1	3.0	2.8

SUMMARY

In summary, the PBMS method has been shown to be capable of measurements of ^{85}Kr samples at an abundance of 6×10^{-9} . APD detectors with 3x higher efficiency for fluorescence detection at 811 nm have been demonstrated. With 10 collectors equipped with two good APD's each, the average total burst size detected from resonant ^{85}Kr atoms would increase from about 2.5 photons to 10 photons. This would make a huge difference in the selectivity and efficiency of the photon burst process. With conditions then more similar to those of our Mg^+ experiments, the full advantage of the photon burst process could be exploited, and measurement of Kr at the ambient air abundance of 1×10^{-11} should be possible.

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