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Reducing potassium contamination for AMS detection of ^{39}Ar with an electron-cyclotron-resonance ion source

P. Collon [a,*], M. Bowers [a], F. Calaprice [b], C. Galbiati [b], D. Henderson [c], T. Hohman [b], C.L. Jiang [c], W. Kutschera [d], H.Y. Lee [c], B. Loer [b], R.C. Pardo [c], M. Paul [e], E. Rehm [c], D. Robertson [a], C. Schmitt [a], R. Scott [c], R. Vondrasek [c]

[a] University of Notre Dame, Notre Dame, IN 46556, USA
[b] Princeton University, Princeton, NJ 08544, USA
[c] Argonne National Lab, Argonne, IL 60439, USA
[d] University of Vienna, Vienna A-1090, Austria
[e] Hebrew University of Jerusalem, Jerusalem 91904, Israel

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ABSTRACT

The first application of ^{39}Ar Accelerator Mass Spectrometry (AMS) at the ATLAS facility of Argonne National Laboratory was to date ocean water samples relevant to oceanographic studies using the gas-filled magnet technique to separate the ^{39}K–^{39}Ar isobars. In particular the use of a quartz liner in the plasma chamber of the electron cyclotron resonance ion source enabled a ^{39}K reduction of a factor ~130 compared to previous runs without liners, and allowed us to reach a detection sensitivity of ^{39}Ar/Ar = 4×10^{-17}. In order to improve this sensitivity and allow the measurement of lower ratios, higher ion source currents and a lower overall ^{39}K background are necessary. This paper summarizes our efforts to investigate new methods combining low level potassium cleaning techniques with the use of ultra-pure aluminum liners in the plasma chamber of the ion source. The aim of the study was to improve by 1–2 orders of magnitude the ^{39}Ar detection sensitivity required in the selection of ultra-pure materials for detectors used in weakly interacting massive particle dark matter searches.

1. Introduction

With an atmospheric isotope ratio of ^{39}Ar/Ar = 8.1×10^{-16} [1], the practical use of ^{39}Ar ($t_{1/2}$ = 269 years) as an environmental tracer represents a major technical challenge. One liter of surface ocean water with an argon solubility of 0.3 cm^3 STP/L contains only ~6500 atoms of ^{39}Ar and produces ~17 ^{39}Ar decays per year corresponding to a specific beta decay rate of ~1 Bq/kg of argon [1]. As long as large ocean water samples (~250 L) were routinely collected for ^{14}C analysis, low level counting (LLC) of ^{39}Ar extracted from four combined water samples (~1000 L) was feasible [2]. However, with the advent of Accelerator Mass Spectrometry (AMS), only 1 L samples were required for ^{14}C measurements, reducing the routine availability of larger volumes of water. As a consequence, the LLC method for oceanographic ^{39}Ar measurements was practically put on hold and no data has been obtained during the past two decades. Therefore it became important to investigate the feasibility of developing a viable AMS technique for ^{39}Ar measurements at facilities such as the Argonne Tandem Linear Accelerator System (ATLAS) facility of Argonne National Laboratory (ANL).

The use of a quartz liner in the Electron Cyclotron Resonance (ECR) ion source of ATLAS reduced the intensity of the interfering ^{39}K isobar background by a factor of ~130. The reader is referred to Ref. [3] for a detailed report of AMS detection of ^{39}Ar using ECR ion sources. The basic principles of which are covered in Ref. [4]. This reduction made the measurement of the ^{39}Ar content in ocean samples possible, pushing the detection limit to ^{39}Ar/Ar ~4×10^{-17}, corresponding to more than four "equivalent half-lives" [3,5]. Repeated testing both at Argonne National Laboratory and at the Université Catholique de Louvain have shown that a limiting factor in the use of quartz liners is the restriction of the overall ion source output of ^{40}Ar^{8+} to ~80 eμA, independent of the quartz quality. However, to achieve ^{39}Ar/Ar ratio measurements with an uncertainty of the order of 5% using no more than 20 L of ocean water samples and in a reasonable experimental time, it was necessary to increase the source beam current as well as to improve the overall detection sensitivity while keeping the ^{39}K background at acceptable levels [6].

Recent work by Calaprice and his group at Princeton has reinforced the need for a further increase in the sensitivity of this

* Corresponding author. Tel.: +1 574 631 3540; fax: +1 574 631 5952.
E-mail address: pcollon@nd.edu (P. Collon).

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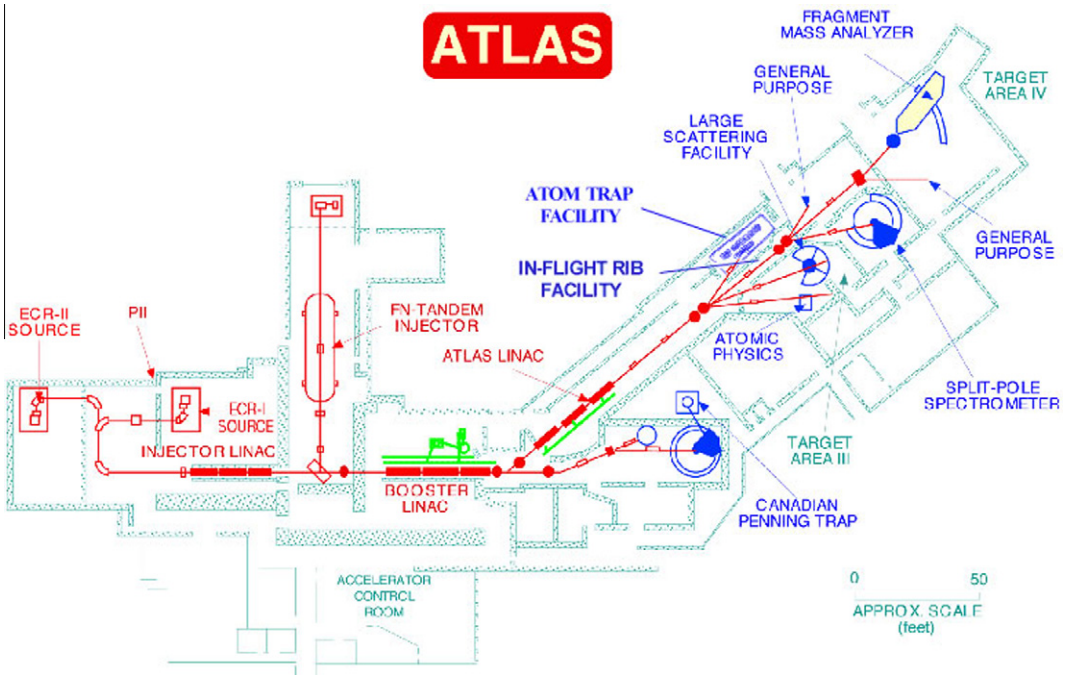

Fig. 1. ATLAS facility floor plan at Argonne National Laboratory. From ECR II to the Split-Pole Spectrometer is approximately 400 feet (120 m).

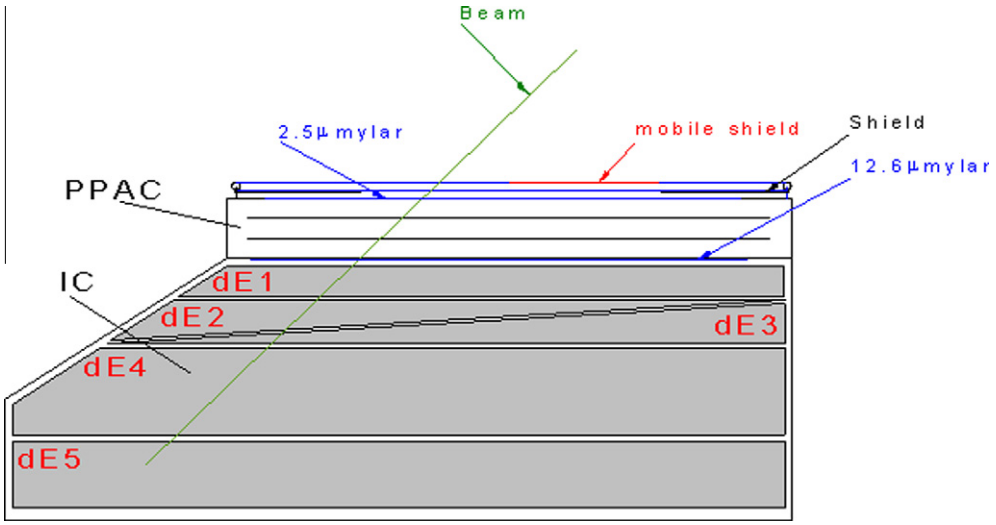

Fig. 2. Typical detector setup with a position sensitive PPAC on top and below an ionization chamber.

AMS technique [7]. The motivation comes from a search for a source of argon that has a concentration of ^{39}Ar at least an order of magnitude lower than that previously achieved. Such an argon source would be useful for new liquid argon detectors currently under development for detecting dark matter Weakly Interacting Massive Particles (WIMPs).

The confirmation of WIMP existence is proposed to be done by studying their collisions with ordinary nuclei and the direct detection of recoil atoms. The recoils will have a continuous energy spectrum ranging up to ~100 keV. The expected event rate could be as low as a few events per ton of detector material per year with a cross section of 3×10^{-45} cm^2. Detecting WIMPs therefore requires a large detector with low background and a low energy threshold. The rare gas atoms – neon, argon, and xenon – have excellent properties for detecting WIMP-induced nuclear recoils. Scintillation properties of argon make this a particularly interesting target material for a large scale WIMP detector [7]. It does however require this argon to be depleted in ^{39}Ar as the background from the β-decay in a large volume argon-based detector would decrease its sensitivity.

Standard liquid argon is obtained from atmospheric argon gas, which as a result of cosmic ray interactions has the natural concentration of ^{39}Ar as given previously. Argon gas is also found underground in natural gas and CO_2 gas wells, originating in part from ^{40}K decay. Because the cosmic ray flux is suppressed, underground argon is generally hoped to be low in ^{39}Ar. However, underground processes can also produce ^{39}Ar through the reaction ^{39}K(n,p)^{39}Ar with neutrons, originating in U and Th traces, mainly through a series of (α,n) reactions. A mantle source of argon may however fulfill experimental requirements. A number of samples were taken from different well sites in the search for a suitable source with an ^{39}Ar concentration below 1% of atmospheric as the desired limit. It

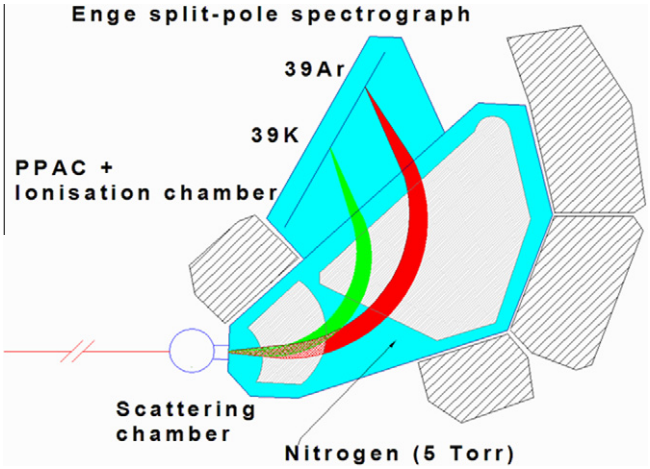

Fig. 3. In the gas-filled magnetic region, the discreet charge states coalesce around a trajectory defined by the mean charge state of the ion in the gas.

was however determined that an AMS measurement was necessary for this level of sensitivity.

2. Experimental considerations

Experimental difficulties associated with the measurement of ^{39}Ar below natural background concentrations of ^{39}Ar/Ar (= 8.1×10^{-16}), are dominated by the interfering stable isobar ^{39}K with a relative mass difference of $\Delta M/M = 1.55 \times 10^{-5}$. The inability of argon to form stable negative ions limits the available accelerator facilities. Production of intense argon beams at the positive ion source ECR2 at ANL (see Fig. 1) with beam currents of ~130 eμA (when the source is run in ultra clean conditions with $^{40}Ar^{8+}$;) will be described later. Assuming a 20% overall beam transmission between the ion source and the detection system, the expected ^{39}Ar count rate at 1% atmospheric concentration is ~1 count every 2 h. Limited statistics at such concentrations require either long running times or increased ion source output. Due to the size and complexity of the ATLAS system (see Fig. 1), ensuring an overall consistent stability in the beam transmission, important in AMS experiments, is highly problematic over extended running times, thus leaving the increase of ion source output, whilst maintaining the interfering isobar ^{39}K output at a minimum, as the most viable solution.

Using a similar method as described in [3], initial system settings and the maximization of beam transmission were obtained using a $^{78}Kr^{16+}$ pilot beam at 464 MeV which has a similar mass-to-charge ratio as $^{39}Ar^{8+}$. Accelerator settings were then scaled to $^{39}Ar^{8+}$ ions at 232 MeV, which were separated from the $^{39}K^{8+}$ isobar and detected using a position sensitive parallel grid avalanche counter (PGAC) backed by an ionization chamber [8,9] (see Fig. 2). The isobaric separation of ^{39}Ar and ^{39}K was achieved using the gas-filled magnet (GFM) technique just prior to the detector [8] (see Fig. 3). In the gas-filled magnetic region isobaric separation is obtained through a combination of the coalescence of each isobar around a mean charge state [10] and the associated energy loss through the gas. The resultant discrete trajectories are strongly dependent on the atomic number of each ion, allowing us to physically block the ^{39}K events before the detector.

Although initial experiments demonstrated a clear separation between the ^{39}K and ^{39}Ar regions of interest, the intensity of the residual ^{39}K at the detection stage created significant signal pile-up in the focal plane gas-filled detector [3]. This level of pile-up was problematic when trying to measure samples at levels below that of atmospheric concentration, as the ^{39}K isobaric background scales with the $^{40}Ar^{8+}$ beam intensity, making an overall beam increase of little use.

Efforts to suppress the isobaric interference focused on reducing its production in the ion source. Extensive testing associated with the inner liner of the ECR plasma chamber found the insertion of a closed quartz liner to be most effective technique [3].

The plasma chamber of an ECR ion source is typically constructed from aluminum which in its untreated state has an aluminum oxide coating. Under bombardment from the plasma ions, the aluminum oxide surface has a high secondary electron yield which enhances the production and stability of the ion source by supplying cold electrons to the plasma. Typically a structural grade, as opposed to a high purity grade, aluminum is used in order to withstand the large forces produced by the permanent magnet hexapole. There are a wide variety of contaminants contained within the bulk structural material which enter the plasma through ion and electron bombardment of the aluminum surface. Liners are utilized to cover the bulk aluminum so that the surface exposed to the plasma is of as high a purity as possible thus reducing the contaminants introduced into the plasma. Quartz liners are advantageous in that they have very few contaminants, they are relatively easy to fabricate, and are transparent to the RF responsible for heating the plasma. The use of the closed quartz liner typically reduces potassium background by a factor of 100; associated heating of the liner however limits in these conditions the maximum achievable $^{40}Ar^{8+}$ beam currents to ~80 eμA. The overall single-charge ionization yield was measured to be 4.4% [3], considerably lower than the ~10% usually expected without a liner. Alternative metal liners or silicon oxide coatings of the plasma chamber (tests conducted at ANL and Louvain-La-Neuve [6]) were repeatedly hampered by extremely high levels of both $^{39}K^{8+}$ and $^{34}S^{7+}$.

Table 1
Summary of results. The ion source current (I_{ECR}) corresponds to the specific current for when the ^{39}K levels were measured. ^{39}K levels are compared to the baseline in line 1 of the table. Higher currents were attained where indicated though transmission was not optimized for these tests, resulting ^{39}K levels unreliable.

Plasma chamber configuration	^{39}K full peak	I_{ECR} ($^{40}Ar^{8+}$)	^{39}K levels Normalized to "Baseline" and beam current	Comments
No treatment (June 2007)	4.2×10^6 cps	83 eμA	Baseline	Measurement made at end of run
Open quartz [3] (Aug 2001)	1.3×10^6 cps	75 eμA	×3.2 reduction	
Closed quartz [3] (May 2002)	9.8×10^3 cps	76 eμA	×430 reduction	Max. reduction but also limited in argon current
Open ultra-pure thin Al liner, no cleaning (June 2007)	4.5×10^4 cps	98 eμA	×110 reduction	Higher beam intensities, high ^{34}S contamination, liner melting
Max beam output achieved in these conditions = 210 eμA				
Ultra-pure Al coated plasma chamber + open quartz + cleaning (April 2008)	1.5×10^6 cps	55 eμA	×1.8 reduction	
Max beam output achieved in these conditions 130 eμA				

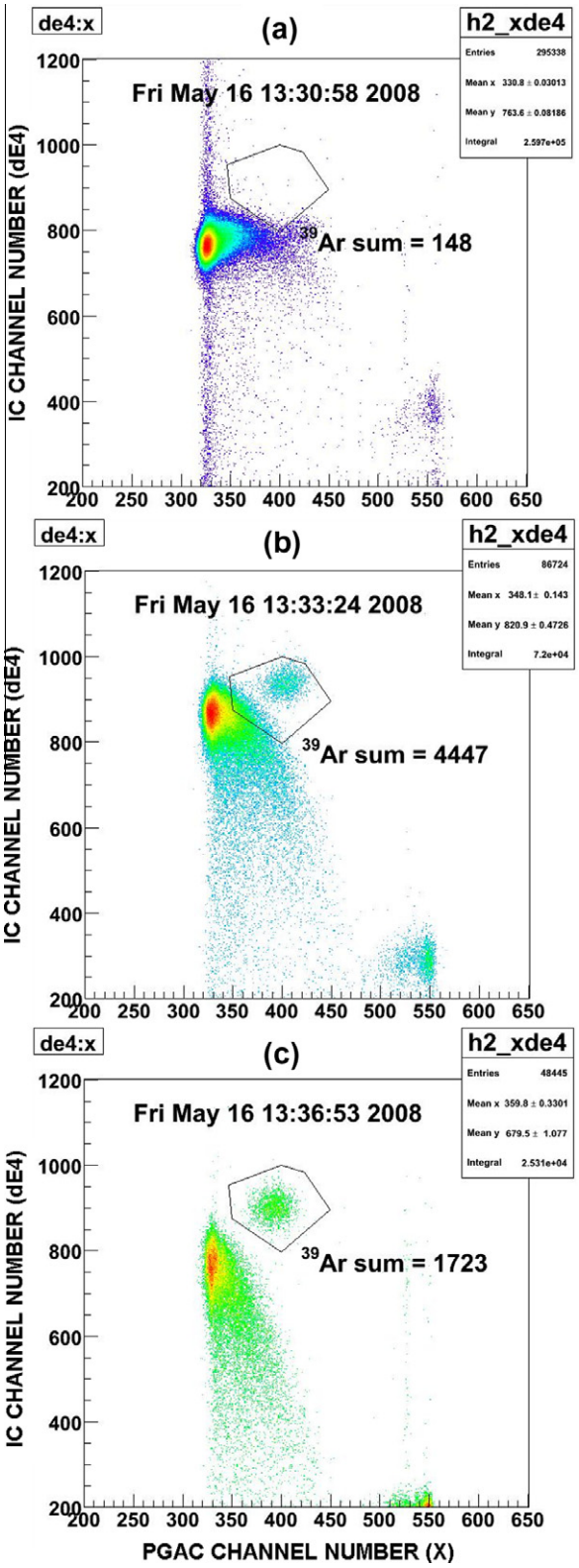

Fig. 4. Position vs dE_4 spectrum shown for varying detector conditions. The 232 MeV $^{39}Ar + ^{39}K$ beam remained constant for panels a, b and c, where a beam block has been placed to minimize most of the ^{39}K peak, with only the tail-end of the peak observed. Panel (a) represents the pressure in the Ionization Chamber P_{IC} = 20.8 Torr. In (b) the pressure is increased to P_{IC} = 24.7 Torr. A greater collection time (approximately 1 h) has resulted in a clearer outline of tailing effects and a more defined ROI for ^{39}Ar ions. The ^{39}Ar - ^{39}K separation achieved is clearly acceptable, however signal pile-up is identifiable as possible interference. In (c) the N_2 pressure (P_{SPEC}) is increased from 12 to 13 Torr resulting in a much cleaner separation between isobars.

3. Isobaric background reduction and rejection techniques

From the large number of measurements performed over a number of years using the ATLAS setup, two development paths to allow for higher beam currents while lowering ^{39}K rates became apparent. The first option was to modify the design of the quartz liner to provide active water cooling necessary for the operation of the ECR source at higher RF power combined with an ultra-pure aluminum coating to be applied to the inside surface. Another path was to use a thick-walled liner of high purity aluminum constructed with an interference fit to the plasma chamber wall to avoid the loss of thermal contact encountered during early testing of metal liners. In view of the results obtained during experiments in 2007 and 2008 it was decided to investigate the second route during an extended beam time in 2009. The results in Table 1 summarize a selection of different measurements made.

3.1. Ion source configurations

Through involvement with the Borexino solar neutrino experiment, Calaprice and his colleagues developed extensive experience in constructing and maintaining low background environments through specific material selection and cleaning techniques. This expertise was utilized at ATLAS in the precision cleaning of critical parts of the ECR ion source through the use of powerful cleaning detergents with very low metal content (e.g. potassium) originally developed by the semiconductor industry for removing both particulates and other contaminants from surfaces. In addition, the ATLAS group and other laboratories working on RF superconductor technology developed and tested high pressure ultra-pure water rinsing techniques. These techniques were used successfully with the ATLAS resonators to remove surface particulates and were adopted by the ATLAS ion source group as a way to reduce potassium concentrations in the plasma chamber.

Initial testing using these techniques was performed in June 2007 with a cleaned, thin-walled (~1 mm) ultra-pure aluminum liner. Resultant $^{40}Ar^{8+}$ output reached 210 eμA measured at the exit of the ECR analyzing magnet, a clear improvement over the quartz liner. For comparison, with no liner, available beam currents had been demonstrated up to 340 eμA of $^{40}Ar^{8+}$, and up to 80 eμA with a quartz liner. These tests were however hampered by extremely high levels of $^{34}S^{7+}$ which made it through the analyzing elements (both magnetic and electrostatic) at both the accelerator and spectrograph, and interfered with the isolation of a clean ^{39}Ar peak in the detector. Subsequently it was found that these high rates were most likely due to the thin ultra pure aluminum liner losing thermal contact with the chamber wall, resulting in a section of the liner melting and the release of contaminants from the bulk material. However, overall lower levels of the ^{39}K count rate (as low as $\sim 3.6 \times 10^4$ cps) demonstrated the possible promise of using aluminum liners.

Further testing in April 2008 was dedicated to potassium reducing techniques using ultra pure aluminum from Hydro Aluminum Deutschland GmbH as a plasma chamber coating agent, thus avoiding thermal contact issues of previous experimental runs. A spare plasma chamber from ECR2 was sent to Princeton University for cleaning and coating of the internal wall with ultra-pure aluminum which had a quoted potassium content of less than 1 ppb (upper limit). Additional ion source components – a new extractor cathode, bias disk, and injector snout – were fabricated out of the same ultra-pure aluminum material. Initial running was performed with an open-ended quartz liner, which was later removed. In both configurations no significant ^{34}S contamination was detected as expected. Although the suppression of ^{39}K was not as effective as previous configurations (comparisons shown in Table 1), the use

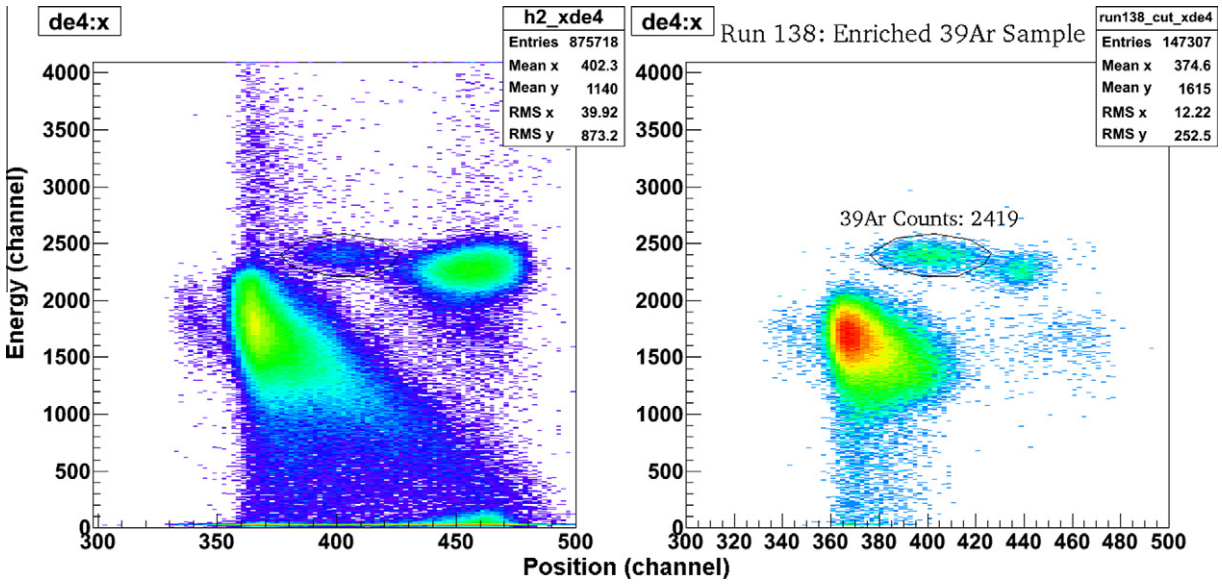

Fig. 5. Enriched argon sample ($^{39}Ar/Ar = 4.6 \times 10^{-13}$). Left: the raw position vs. dE_4 spectrum. Right the same spectrum gated on time-of-flight. Run time: 613 s (90% live), source current = 76 eμA. The peak on the right of the spectrum (~470 × 1500) corresponds to the tail end of the ^{34}S peak making it through the accelerator and the gas-filled dipole.

of an ultra-pure aluminum-coated plasma chamber showed definitive ^{39}K reduction when compared to a bare chamber whilst still maintaining high argon output currents of ~130 eμA.

3.2. Improved detector sensitivity

The reduction of the ^{39}K isobaric contamination was also coupled with the improvement of the detection system sensitivity. Modifications to the Mylar window support grid allowed for an increase in detector gas pressure and subsequent greater separation of ^{39}K and ^{39}Ar regions of interest (ROIs). Due to the specific ranges of these isobars in the detector gas, the slight change in gas pressure is sufficient to move the ^{39}Ar peak away from the tailing ^{39}K interference (see Fig. 4).

The three spectra shown in Fig. 4 are from 232 MeV ^{39}Ar ions with accompanying isobaric contamination originating from an atmospheric argon sample. The majority of the interfering ^{39}K isobar has been blocked from the detector through the presence of a hard edge at ~ channel 325, leaving only the tail as interference. The gas pressure conditions shown in (b) (P_{IC} = 24.7 Torr) shows clear separation of the two peaks, however a large visible spread in peak width limits any further increase. Maintaining detector pressure and increasing magnet gas pressure from 12 Torr (b) to 13 Torr (c) helps to both separate peaks further and reduce visible spread in both peaks.

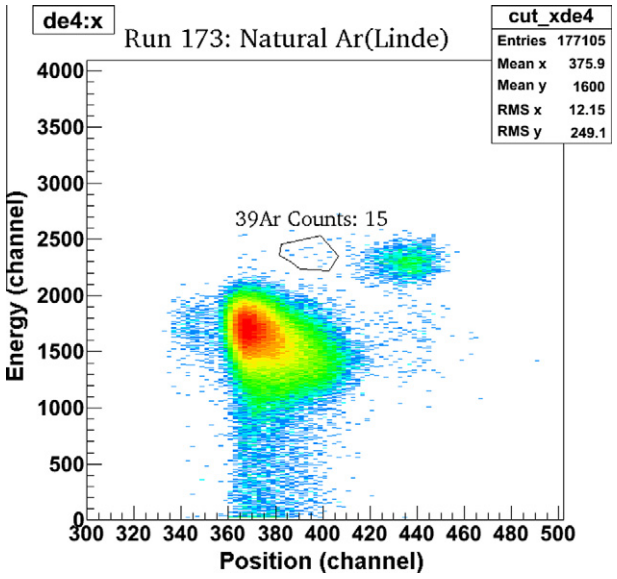

Fig. 6. Natural argon sample ($^{39}Ar/Ar = 8.1 \times 10^{-16}$). Run time 1964 s, source output = 66 eμA.

4. Implementation and ^{39}Ar measurements

As the final goal of this study was the measurement of $^{39}Ar/Ar$ ratios well below the previously reached level of 4×10^{-17}, a combination of all the previously outlined techniques was deemed necessary – precision cleaning, the use of ultra-pure materials, increased beam currents (predicted around 200 eμA), and better detector precision in isobar separation.

Starting with the reduction of background production, a thin layer of material was milled off the inner surface of the ECR ion source aluminum plasma chamber in order to remove possible implanted impurities from previous experimental runs. The chamber was then transported to Astro Pak (Downey, CA) for specialized ultra-low potassium cleaning. A 5 mm ultra-pure aluminum liner from Hydro Aluminum Deutschland GmbH was then interference-fitted inside the chamber; all procedures were maintained at level 10 clean-room specifications.

We observed however that in spite of the extreme measures taken to insure high purity materials and clean conditions the ^{39}K isobaric intensity could not be reduced to levels allowing us to measure reliably concentrations below atmospheric ($^{39}Ar/Ar$ ratio of 8.1×10^{-16}). Tests using different support gasses, various microwave rf injection schemes, and beam chopper settings did not allow us to reduce the level of the ^{39}K contamination backgrounds in any significant way. In the best available experimental conditions, the measurement of a neutron activated sample ($^{39}Ar/Ar$ ratio of $(4.6 \pm 0.2) \times 10^{-13}$) and a natural sample was possible, (see Figs. 5 and 6). However, a consistently high ^{39}K background (see Fig. 7) made measurements below this impossible.

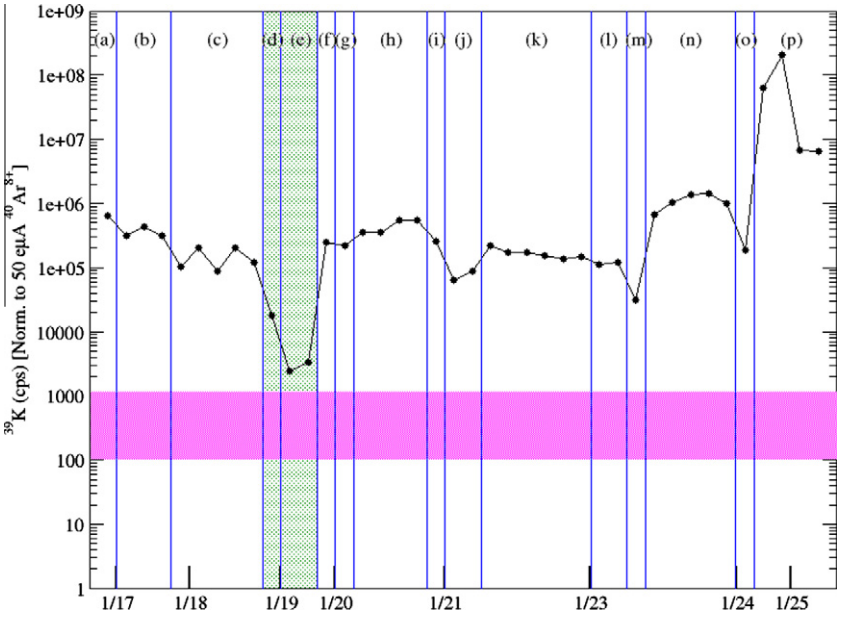

Fig. 7. Summary of potassium count rate (counts per sec, cps) at the detector (normalized to 50 eμA of $^{40}Ar^{8+}$ at the ion source) as a function of different ion source support gasses and conditions during the 2 week January 2009 run. All argon used for these runs was natural. The red area (horizontal shaded region) represents the potassium count rate required to reach $^{39}Ar/Ar$ levels below 4×10^{-17} and the green shaded area (vertical shaded region) represents a time period where no accelerator re-tuning was performed and the overall transmission decreased by up to two orders of magnitude. Retunes are based on krypton injection into the source and using $^{78}Kr^{16+}$ as a pilot beam. The experimental time span covers a total of 9 days. (a) He support + natural Argon in ECRII; (b) He + Argon (Linde). All following runs were made using the Linde Ar supply. (c) Boil-off N_2 support + Ar; retune of ion source only; (d) attempt at accelerator re-tune on K count rate only; (f) retune of ATLAS using the Kr pilot beam; (g) after the enriched Ar sample (see text); (h) high purity N_2 support + Ar; (i) after an Ar shut-off; (j) after increasing the Ar pressure in the source; (k) after ATLAS retune on krypton; (l) After removal of the HP aluminum liner and installation of the Notre Dame quartz liner (Kr retune, N_2 + Ar); (m) source re-tune; (n) full ATLAS retune; (o) N_2 + Ar check during rf-tests on ion source (see text); (p) after removal of all liners (2 last points are after 1 night of ion source conditioning but with NO krypton re-tune).

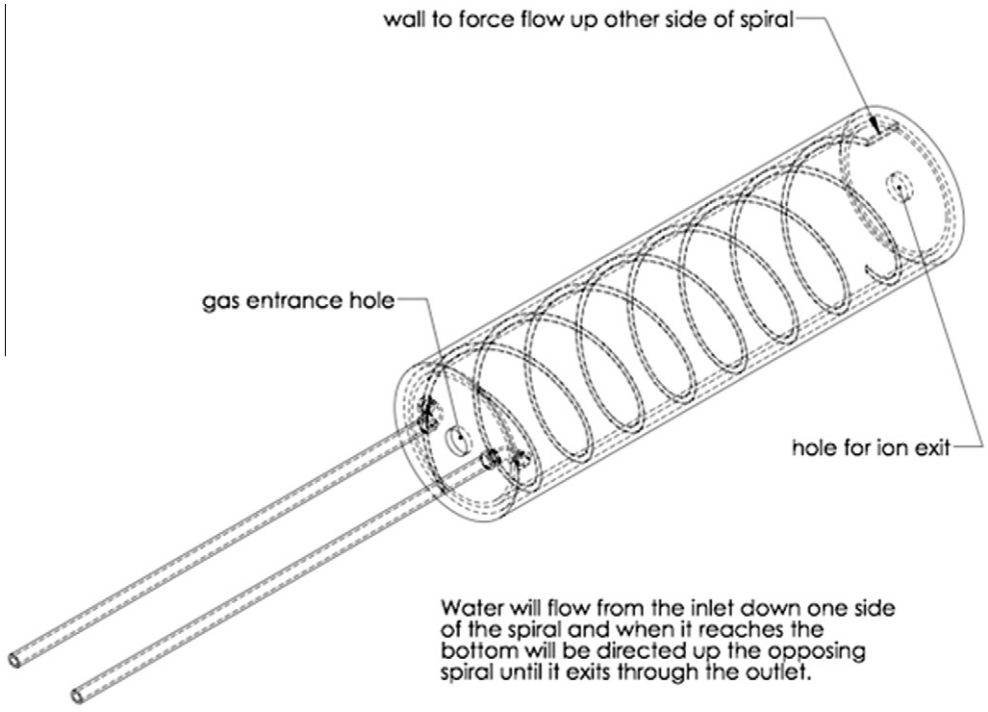

Fig. 8. A schematic of the closed quartz liner that is actively cooled.

5. Conclusions and possible outlooks

It seems clear at this point that even the combination of low-potassium cleaning techniques and ultra-pure aluminum liners does not provide the necessary low potassium levels required for measurements of ^{39}Ar well below the natural level using a general purpose ECR ion source. Even so-called ultra-pure metals contain high enough trace concentrations of potassium to result in significant beam background when they are used in the plasma chamber of an ECR ion source. Though copper would provide a higher purity

than aluminum, it does not allow for the production of high enough ion beam intensities due to its lower secondary electron yield. As previous testing has shown, well conditioned quartz liners provide the low potassium levels needed, however, the low overall output of the ion source using these liners precludes the measurements at and below the 10^{-17} level.

A possible development path at this point requires the development of a stand-alone ECR ion source constructed of high-purity materials with a quartz liner that is aluminum coated and actively water cooled. The best results in terms of potassium background have always come with the closed ended quartz liner, and the hope is that the aluminum coating will allow us to increase the source output (see Fig. 8). This development is however non-trivial and will require extensive research at an off-line ECR source not currently available at ATLAS.

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