Nuclear Instruments and Methods in Physics Research B 123 (1997) 122–127

NIM B
Beam Interactions with Materials & Atoms

ELSEVIER

Measurement of ^{81}Kr in the atmosphere

P. Collon [a,*], T. Antaya [b], B. Davids [b], M. Fauerbach [b], R. Harkewicz [b], M. Hellstrom [b], W. Kutschera [a], D. Morrissey [b], R. Pardo [c], M. Paul [d], B. Sherrill [b], M. Steiner [b]

[a] *Institut für Radiumforschung und Kernphysik der Universität Wien, Boltzmanngasse 3, 1090 Vienna, Austria*
[b] *Cyclotron Laboratory, Michigan State University, East Lansing, MI 48824, USA*
[c] *Physics Division, Argonne National Laboratory, Argonne, IL 60439, USA*
[d] *Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem, Israel 91904*

Abstract

We present the first AMS measurement of the ^{81}Kr concentration in atmospheric krypton. The measurement was performed by combining positive-ion production in an electron cyclotron resonance source with acceleration to high energy in a cyclotron and subsequent full stripping for ^{81}Br–^{81}Kr separation. The result, $^{81}Kr/Kr = (5.3 \pm 1.2) \times 10^{-13}$, agrees well with two previous low-level decay counting measurements.

1. Introduction

The use of radionuclides is developing into a major tool in environmental research and it is therefore important to understand their distribution, production mechanism and geochemical behaviour. Long-lived noble gas radionuclides could play a particularly important role in this field as they are chemically inert and, as a consequence, their geochemical behaviour and distribution on earth is simpler than that of reactive elements. The present experiment is part of a program to develop AMS for long-lived noble gas radionuclides [1].

At the AMS conference in Niagara-on-the-lake, Oeschger pointed out [2] that ^{81}Kr could be an ideal tracer due to its unique geochemical and geophysical properties:

(1) ^{81}Kr has a half-life of $t_{1/2} = 210000$ a and is produced in the atmosphere by cosmic-ray induced spallation and neutron activation of stable krypton. The atmosphere can be considered as the only major reservoir of ^{81}Kr on earth. In addition, due to its long half-life, short term fluctuations in the cosmic ray intensities and therefore in the production rate of ^{81}Kr, are smoothed out. With the assumption of secular equilibrium and a $^{81}Kr/Kr$ ratio of 5.9×10^{-13} [3], a global production rate of 1.5×10^{-6} ^{81}Kr atoms cm^{-2} s^{-1} can be estimated [1].

(2) There is little if any contamination of natural ^{81}Kr from anthropogenic sources. In atmospheric nuclear testing, ^{81}Kr can be produced via the reactions ^{80}Kr(n, γ)^{81}Kr (σ_{therm}(n, γ) = 11.5 barn) and ^{82}Kr(n, 2n)^{81}Kr, and through the fission of uranium and plutonium. The (n, γ) contribution was estimated from the doubling of atmospheric ^{14}C during nuclear testing, the (n, 2n) contribution from the limit of anthropogenic ^{40}Ar(n, 2n)^{39}Ar production given in Ref. [4], and the fission contribution by assuming a total equivalent power of 500 Mton TNT released in the atmospheric tests. These estimates lead to $^{81}Kr_{bomb}/^{81}Kr_{nat}$ ratios of 10^{-3}, 10^{-4}, 10^{-7}, respectively. The contribution from fission is particularly well suppressed because ^{81}Kr is shielded by stable ^{81}Br from β-decay feeding through more neutron-rich mass-81 fission products. The direct ^{81}Kr fission yield has been estimated to be as low as 7×10^{-11} [5].

In particular, ^{81}Kr is probably the only cosmogenic radionuclide which has the potential of developing into a reliable absolute chronometer for dating old ice from polar ice sheets as well as old groundwater. Whereas first measurements of ^{81}Kr were performed with Low Level Counting techniques (LLC) this is not possible anymore due to the high β-decay background of anthropogenic ^{85}Kr ($t_{1/2}$ = 10.7 a) originating from the nuclear industry. The estimated pre-nuclear $^{85}Kr/Kr$ ratio of 3×10^{-18} has increased to a present day ratio of about 1.3×10^{-11} [6,7]. In addition LLC would require large sample sizes and these are not always available, especially for the dating of deep ice cores. AMS offers new and exciting possibilities for measuring ^{81}Kr concentrations and our efforts have been oriented at developing a viable counting technique for ^{81}Kr. However due to the low atmospheric concentrations of ^{81}Kr ($^{81}Kr/Kr = 5.2 \times 10^{-13}$) it is estimated that only approximately 1500 ^{81}Kr atoms are contained in the

* Corresponding author. Fax +43 1 407 6200, e-mail collon@pap.univie.ac.at.

PII S0168-583X(96)00674-X

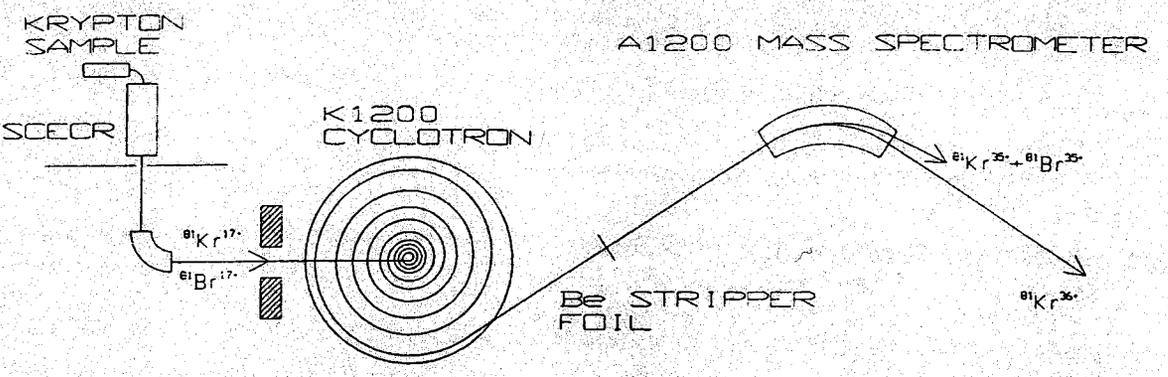

Fig. 1. Schematic view of the experimental set-up at Michigan State University. The superconducting ECR (SCECR) source coupled to the K1200 cyclotron and the A1200 mass spectrometer is used in an attempt to separate the ^{81}Kr–^{81}Br isobars using full stripping at high energies. For acceleration and detection purposes the $^{81}Kr^{17+}$ charge-state was selected and accelerated to an energy of 45 MeV/A. A Be stripper foil (18.8 mg/cm^2) provided a 70% stripping efficiency for the 36+ charge state. The ions emerging from the foil were analysed in the A1200 mass separator.

trapped air bubbles of one kilogram of modern ice and therefore a very high overall efficiency would be required for investigation of these interesting samples with AMS.

2. Use of positive ion sources for the production of krypton ions

The main barrier to using noble gases in AMS is the instability of negative ions which makes them unsuitable for measurements with tandem accelerators. Nevertheless the development of positive ion sources, in particular Electron Cyclotron Resonance (ECR) ion sources coupled to an accelerator, opened up new possibilities.

The principal experimental difficulty in developing a viable AMS counting method for ^{81}Kr resides in the separation of the ^{81}Kr and ^{81}Br isobars ($\Delta M/M = 3.7 \times 10^{-6}$). A possible method for the isobar separation is full stripping at high energies. This technique leads to a clean isobar separation although one must take into account that nuclear reactions of ^{81}Br beam particles with the stripper foil material produce ^{81}Kr (e.g. through the $^{9}Be(^{81}Br, ^{81}Kr)^{9}Li$ reaction). It was decided [1] to use the superconducting ECR (SCECR) source coupled to the K1200 cyclotron and the A1200 mass separator of Michigan State University in an attempt to rid ^{81}Kr of its ^{81}Br background (Fig. 1). Natural krypton and neutron activated krypton sample material were available in 100 cm^3 quartz am-

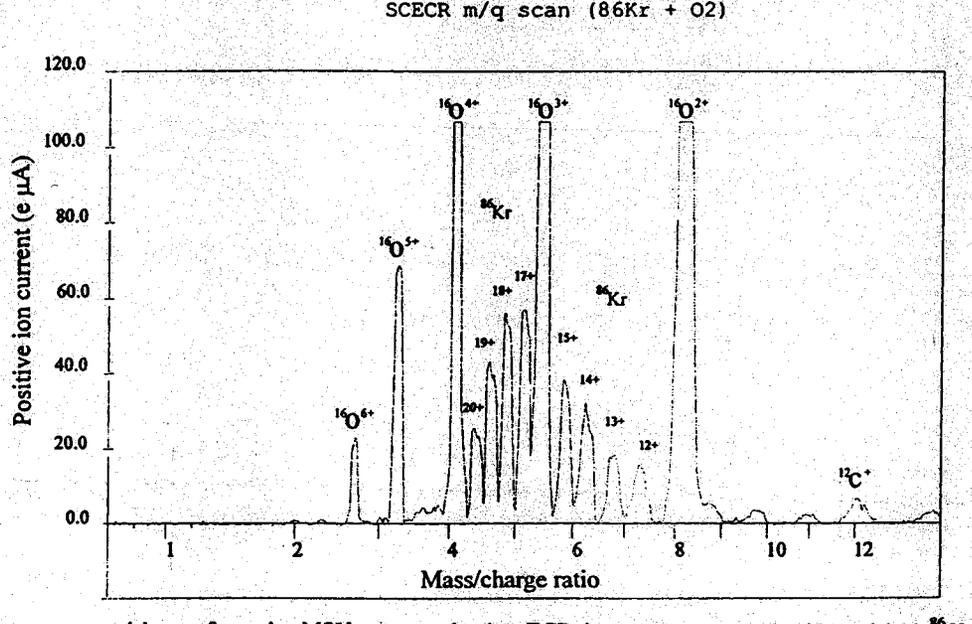

Fig. 2. Ion current versus mass/charge from the MSU superconducting ECR ion source operated with enriched ^{86}Kr gas and oxygen support gas.

poules as well as a highly enriched (> 99%) ^{86}Kr sample which was mainly used for beam set-up. The krypton sample material and the support gas were introduced into the ion source plasma through two separate, remotely controlled needle valves. This system coupled to a vacuum pump and valve permitted to change sample-gas ampoules without affecting the ion source settings. Due to the lack of absolute pressure transducers in this system, it was only possible to roughly estimate the krypton gas consumption rate. An upper limit of ~ 1 cm^3 STP per hour was established, but the actual consumption may well be considerably lower (see Section 5 for planned improvements). A spectrum of the charge-state distribution after extraction from the ion source is given in Fig. 2.

3. Experimental set-up

The experimental set-up was the same as the one described in Ref. [1]. For acceleration and detection purposes the $^{81}Kr^{17+}$ charge state had been selected for three reasons: (1) the source output was high; (2) an energy of 45 MeV/A was used, because it was within the stable region of the rf-magnetic field parameter space of the cyclotron, and it provided a high fraction of fully stripped ions [1]; (3) there are no background components, relative to the $^{81}Kr^{17+}$ ion beam, with a mass-to-charge ratio degeneracy within the bandwidth (2.8×10^{-4} $\Delta(M/Q)$) of the cyclotron, except for ^{81}Br that is not eliminated in the acceleration process due to its $\Delta(M/Q)$ of 3.7×10^{-6}. Between the exit of the cyclotron and the A1200 mass spectrometer, a Be stripper foil (18.8 mg/cm^2) provided a 70% stripping efficiency for the 36+ charge state. The ions emerging from the foil were analysed in the A1200 mass separator and were finally detected in 2 $\Delta E - E$ telescopes (75 μm, 100 μm, 500 μm, 1000 μm Si detectors). An additional time of flight information was provided by a scintillator placed after the first bending magnet of the spectrometer. The source output current ($^{84+86}Kr^{17+}$) was measured in a Faraday cup placed after the ion-source analysing magnet. During the 1994 run, the reconfigured A1200 was operated in a high resolution mode thereby improving the mass separation of the ^{81}Kr beam from the ^{81}Br reaction products in the stripper foil as compared to previous runs [1].

Acceleration of $^{81}Kr^{17+}$ ions was set-up by first tuning the cyclotron with a $^{86}Kr^{18+}$ ion beam. Subsequently the cyclotron frequency was shifted from $^{86}Kr^{18+}$ to $^{81}Kr^{17+}$ by an amount corresponding to their M/Q difference of 0.27%.

The A1200 mass spectrometer was set to accept ions with an M/Q ratio of 81/36, easily separating fully stripped $^{81}Br^{35+}$ and $^{81}Kr^{36+}$ ions. Nevertheless the high $^{81}Br^{17+}$ background induces reaction products in the stripper foil that heavily dominate in the final spectrum (Fig. 3). Previous experiments had severely been hampered by this background and therefore one of the first objectives was to try to identify and reduce the source of bromine in the SCECR before the acceleration process. Only a reduction by several orders of magnitude would permit the measurement of natural krypton samples. As the A1200

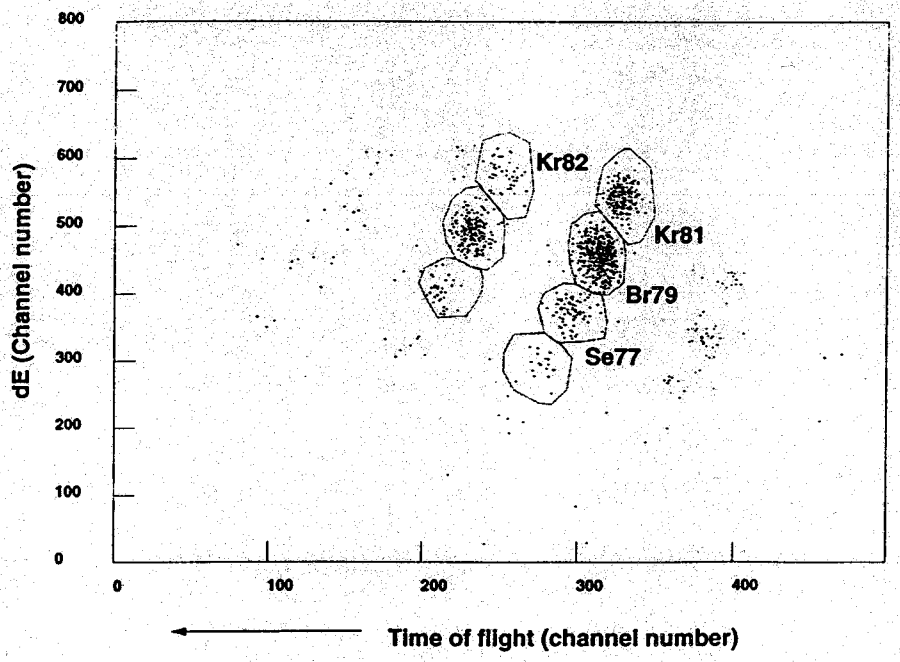

Fig. 3. ΔE versus TOF spectra measured with the A1200 mass-separator after mass-81 ions of 45 MeV/A are stripped in an 18.8 mg/cm^2 thick beryllium foil. The identified groups correspond to reaction products induced in the Be foil by the $^{81}Br^{17+}$ background. The sample used was a neutron activated krypton sample ($^{81}Kr/Kr = 2.2 \times 10^{-10}$).

effectively eliminated the $^{81}Br^{35+}$ ions it was not possible to directly monitor the bromine background and the ^{79}Br counts were therefore used during the experiment, as a monitor for the contribution of nuclear reaction products from interactions of ^{81}Br with the Be stripper foil.

As the support gas in the SCECR was considered a possible source of bromine, it was decided to place a dry-ice cold trap on the support gas line in an attempt to freeze out any possible bromine contaminants. For set-up and tuning purposes, oxygen had been used as a support-gas and first measurements with the cold trap clearly showed a reduction in the bromine background. It was therefore decided to try argon as a support-gas and, although the krypton current was thereby reduced by 25%, the bromine background was clearly reduced by an order of magnitude. Furthermore this mode provided an unexpected additional reduction of the bromine background: As previously mentioned krypton was fed into the SCECR simply by remotely opening a needle valve. With this method it was possible to study the effect of the krypton gas on the source output as well as on the background count rate, without changing the settings of the source. First measurements of the bromine count rate at the focal plane of the mass spectrometer were made without krypton being supplied to the source in an attempt to obtain a baseline on the bromine background originating from the ion source. After this, the valve was opened, thereby transferring krypton gas into the ion source plasma without changing any source settings. The effect was dramatic: the bromine background count rate dropped by an order of magnitude, as if in this mode krypton suppresses bromine in the source. This measurement was repeated several times during the experiment and the effect was clearly reproducible. This effect may be due to the particularity of gas mixing effects in the ECR sources.

4. Experimental results

After reducing the bromine background by two orders of magnitude it was possible to attempt first measurements of natural krypton samples (Fig. 4) as well as various neutron activated krypton samples (sample #1 $^{81}Kr/Kr = (2.2 \pm 0.2) \times 10^{-10}$, sample #2 $^{81}Kr/Kr = (1.4 \pm 0.2) \times 10^{-11}$). The ^{81}Kr concentration in the latter samples was determined by measuring the gamma activity of short-lived Kr isotopes and relating it to ^{81}Kr with the corresponding neutron capture cross sections. Table 1 summarises the $^{81}Kr/Kr$ measurements with enriched and natural samples that were made at the Michigan State University Cyclotron Laboratory in 1994.

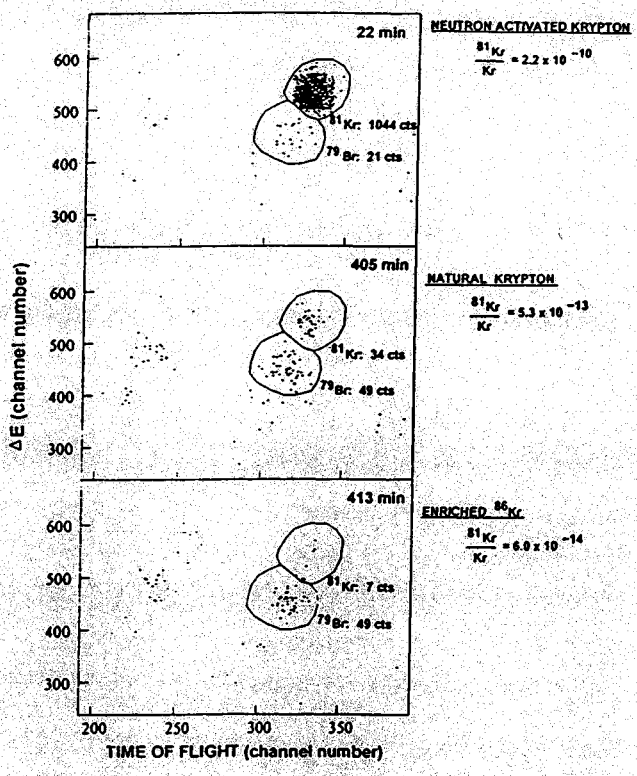

Fig. 4. Particle identification spectrum measured with the A1200 fragment separator when the system was optimised for $^{81}Kr^{36+}$ detection. The ^{79}Br counts are indicative for the contribution of nuclear reaction products from interaction of the ^{81}Br background beam with the Be stripper foil. A ratio of $^{81}Kr/^{79}Br = 1/16$ was found from measurements with no krypton gas in the SCECR. This factor was used to determine the contribution of ^{81}Kr from reaction products and normalised to the observed ^{79}Br counts.

In order to determine the proportion of ^{81}Kr background that originates from reaction products, a 30 min run was made with the krypton-sample gas valve closed. The resulting ratio of $^{79}Br/^{81}Kr = 15.9 \pm 1.1$ was used to

Table 1
Summary of the $^{81}Kr/Kr$ measurements

Sample	$^{81}Kr/Kr$	$^{84+86}Kr^{18+}$ (eμA)	Total ^{81}Kr (counts)	Background [a] (counts)	Run time (min)	$^{81}Kr/Kr$ measured [b]
n-act	$(2.2 \pm 0.2) \times 10^{-10}$	28.5	1044	1	22	ref. value
n-act	$(1.4 \pm 0.2) \times 10^{-11}$	17.2	373	16	219	$(1.3 \pm 0.2) \times 10^{-11}$
natural	$(5.2 \pm 0.6) \times 10^{-13}$ [c]	19.3	34	3	405	$(5.3 \pm 1.2) \times 10^{-13}$
^{86}Kr	depleted in ^{81}Kr	21.3	7	3	413	$(6.0 \pm 4.8) \times 10^{-14}$

[a] The background was determined from measurements with the Kr sample gas turned off. [b] $^{81}Kr/Kr$ ratios are determined relative to the reference value of 2.2×10^{-10}. Uncertainties are statistical only. [c] This value is the average of $(5.9 \pm 0.6) \times 10^{-13}$ [3] and $(4.5 \pm 0.3) \times 10^{-13}$ [10].

determine the contribution of reaction products (normalised to the observed ^{79}Br counts) to the ^{81}Kr count rate.

The excellent agreement between the AMS measured $^{81}Kr/Kr$ ratio and the accepted concentration in the atmosphere, encourages us to continue our measurements. However, considering the small number of ^{81}Kr events actually detected, we view this agreement as somewhat accidental, and at this time do not take it as a firm proof that modern krypton has the same isotopic abundance of ^{81}Kr as the pre-nuclear value of $^{81}Kr/Kr = (5.2 \pm 0.6) \times 10^{-13}$.

5. Multiple sample gas handling system

As previously mentioned, one of the problems when developing counting techniques for ^{81}Kr remains the sample size, especially when dealing with krypton samples originating from deep ice cores where it is not possible, for economical and practical reasons, to obtain large samples. It was therefore decided to develop a system capable of handling and delivering to the ion source small gas samples (≈ 1–3 cm^3 STP). The basic concept was adapted from the Oxford CO_2 gas source [9] comprising the following features:

(1) It should handle four different gas samples allowing sample changes with little loss of time and without affecting the settings of the ion source.

(2) It should suppress any bromine present in the sample, through the use of a cold trap. As krypton and bromine respectively have melting points of -156.6°C and -7.2°C it was decided to suppress any bromine present in the sample by freezing it out.

(3) It should be transportable and adaptable to any ECR source.

The system consists of two sections (Fig. 5): One, at ground potential that handles the initial sample preparation and the second part, at source potential that handles the freezing-out and transfer of the sample gas to the ion source. Each of the four quartz ampoules of ≈ 4 cm^3 volume, containing the krypton samples, is placed in one of the flexible sample holders. After having been evacuated, these holders allow the ampoules to be broken, thereby releasing the sample gas. The sample gas can then be released into the system where it is transported to the cold trap with the help of helium as support gas. The cold trap is cooled by liquid nitrogen, thereby freezing out the sample gas together with any possible bromine contaminants. The helium is then evacuated from the cold trap and through controlled heating, the krypton can be released into the ion source while retaining the bromine in the trap. The whole procedure is computer controlled with a PC-

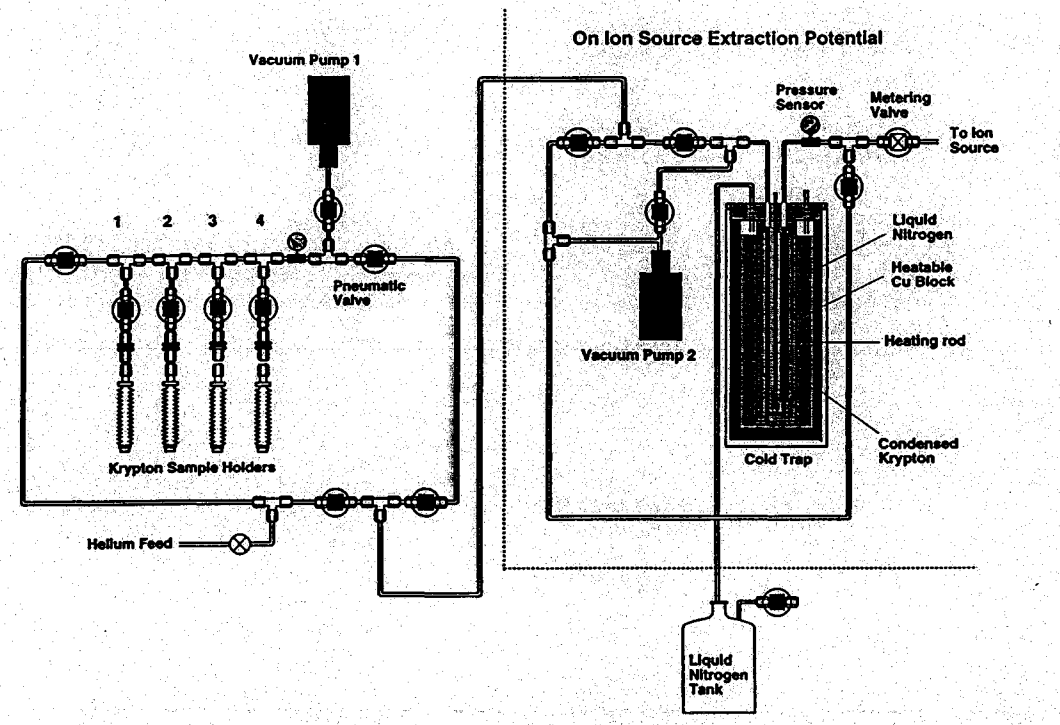

Fig. 5. Schematic view of the multiple-sample gas handling system developed for handling small krypton gas samples. The samples are supplied in sealed quartz ampoules of ~ 4 cm^3 volume to the flexible sample holders, where they can be broken under vacuum. The sample gas is transported with helium as support gas to the cold trap, where it is frozen out together with any possible bromine contaminant. Through controlled heating of the trap, krypton can be released to the ion source while retaining the bromine, thus reducing the ^{81}Br interference for the ^{81}Kr detection. The gas transfer procedure is computer controlled with a PC-based software program. The controls for the system-part that is at source extraction potential ($\sim +13$ kV) is made possible thanks to the use of optic fibre cables.

based software program. First on-line tests, of this system coupled to the Michigan State University SCECR in 1995 were satisfactory, although certain improvements still have to be made to optimise the freezing out process. In order to determine the gas consumption of the ECR source it will also be necessary to replace the pressure transducer in the cold trap with one that provides absolute pressure readings.

6. Conclusions

The results in Table 1 are very encouraging, although work still has to be done in order to eliminate the ^{81}Br background and in understanding the gas mixing effects in the ion source. One aspect that has to be investigated is the choice of stripper target as different foils may eliminate some of the reaction products that hamper the final spectrum. Nevertheless one of the main difficulty still remains: improving the overall detection efficiency. Most interesting samples contain only several thousand atoms at most and a high overall detection efficiency is required for investigation of such samples.

First tests with the gas handling system are very promising although improvements still have to be made in order to optimise the transfer and freezing out process. Future runs at Michigan State University are planned.

References

[1] W. Kutschera, M. Paul, I. Ahmad, T.A. Antaya, P.J. Billquist, B.G. Glagola, R. Harkewicz, M. Hellstrom, D.J. Morrissey, R.C. Pardo, K.E. Rehm, B.M. Sherrill and M. Steiner, Nucl. Instr. and Meth. B 92 (1994) 241.
[2] H. Oeschger, Nucl. Instr. and Meth. B 29 (1987) 196.
[3] H.H. Loosli and H. Oeschger, Earth Planet. Sci. Lett. 7 (1969) 67.
[4] H.H. Loosli, Earth Planet. Sci. Lett. 63 (1983) 51.
[5] T. Florkowski, L. Morawska and K. Rozanski, Nucl. Geophys. 2 (1988) 1.
[6] W. Weiss, H. Stockburger, H. Sartorius, K. Rozanski, C. Heras and H.G. Ostlund, Nucl. Instr. and Meth. B 17 (1986) 571.
[7] F. von Hippel, D.H. Albright and B.G. Levi, Sci. Am. 253 (1985) 40.
[8] T.A. Antaya, J. Phys. (Paris) C1-50 (1989) 707.
[9] C.R. Bronk and R.E.M. Hedges, Nucl. Instr. and Meth. B 52 (1990) 322.
[10] V.V. Kuzminov and A.A. Pomansky, Proc 18th Int. Cosmic Ray Conf., Bangalore, India, Vol 2 (Int. Union Pure and Applied Physics, 1983) p. 357.