Development toward a double focusing isotopic separator for noble gas isotope enrichment

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A double focusing sector field mass filter used in Nier–Johnson geometry has been built in order to perform Kr isotope enrichment for ^{81}Kr and ^{85}Kr isotopes. The principle consists in implanting Kr$^+$ ions accelerated at 7 keV in Al foils after separation using the magnetic sector. A specific ion source has been designed capable of generating high Kr$^+$ ion beams ($>0.5\,\mu$A) to transfer into the collecting Al foils in 3 to 5 h significant fractions of large Kr samples (10^{15} to 10^{16} atoms) initially introduced in the instrument. Implanted Kr isotopes can be further selectively released from the Al foil by surface ablation using an infrared laser beam. Implantation yields and enrichment factors are measured using a conventional mass spectrometer. Copyright © 2016 John Wiley & Sons, Ltd.

Introduction

Radioactive isotopes of noble gases are considered as powerful and sensitive tracers for environmental studies. In particular, ^{85}Kr (half-life 10.76 years), ^{39}Ar (269 years) and ^{81}Kr (229,000 years) have been used for age dating of groundwaters[1–8] and polar ice sheets,[9] for studying transport processes in the oceans,[10,11] and the atmosphere, for monitoring nuclear fuel reprocessing activities[12–14] and for checking ^{85}Kr radioactivity in solar neutrino detector systems.[15,16]

Because of their chemical inertness, noble gases have the great advantage to be easily extracted with high efficiency from a large quantity of environmental samples (atmosphere, water, ice). However, their extremely low concentration in environmental samples implies the implementation of very sensitive and sophisticated detection techniques.

In this work, we focus on the two long-lived krypton radioisotopes both present in the atmosphere, ^{81}Kr that is mainly cosmogenic in origin and ^{85}Kr that is essentially an anthropogenic nuclear fission product released by nuclear fuel reprocessing facilities.

The instrumental development reported in this work is a part of a wider project aiming at the development of a method for ultrasensitive determination of isotopic abundances of ^{81}Kr and ^{85}Kr extracted from environmental samples (1 l of atmosphere and less than 20 l of groundwater or ice sheet).

The analytical methodology is composed of three steps: (1) krypton extraction from environmental samples and purification, (2) isotopic enrichment in ^{81}Kr and ^{85}Kr with respect to other Kr isotopes and (3) measurement of the abundances of the two isotopes of interest.

This paper deals with the second step, i.e. development of a high efficiency isotopic separator. The third step of the project consists in the development of an ultrahigh sensitivity spectrometer for the measurement of Kr isotopes. The instrument is now operating[17] with a detection limit of about 500 atoms for any Kr isotope. It is based on a resonance ionization source using UV laser pulses coupled with time of flight mass analyzer (RIS-TOF).

In addition to their extremely low abundance, another major issue for the detection of these isotopes arises from their very low abundance ratio relatively to the other non-radioactive Kr isotopes, about 5×10^{-13} and 2×10^{-11} for ^{81}Kr/Kr and ^{85}Kr/Kr respectively.[18] As a consequence, because of the well-known 'peak tail effect' (i.e. diffusion of the ion beams onto adjacent masses caused by residual gas in the mass spectrometer), signals detected at the mass to charge ratios (m/z) of the ^{81}Kr and ^{85}Kr isotopes are mainly because of ions coming from neighboring isotopes (mainly ^{80}Kr and ^{82}Kr ions at m/z of ^{81}Kr, and ^{84}Kr and ^{86}Kr ions at m/z of ^{85}Kr). Moreover, the quantity of atoms that can be introduced in the RIS-TOF instrument for step (3) must not exceed ~10^7–10^8 atoms because of a space-charge limit into the source. To overcome these problems, one possible approach consists in proceeding to a significant isotopic enrichment of ^{81}Kr or ^{85}Kr relatively to other Kr isotopes with minimum ^{81}Kr and ^{85}Kr losses.

In 1987, Lehmann et al.[19] first developed a Wien mass filter enrichment system as a first requirement for the isotope abundance measurement of krypton isotopes. Following a similar approach, a double focusing isotopic separator has been developed at Centre d'Etudes Nucléaires de Bordeaux-Gradignan (CENBG) for efficient separation of Kr isotopes and implantation into Al foils.

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Other methods are currently used for [81]Kr and/or [85]Kr measurements. Low level decay counting is performed routinely in a few specialized laboratories around the world[20,21] for measuring [85]Kr in cubic-meter size samples. Because of the low activity of [81]Kr, detection is mostly based on counting atom method. Significant efforts have been made on atom trap trace analysis (ATTA), capable of detecting both [81]Kr and [85]Kr in environmental samples.[22] An atom of a particular isotope is selectively captured by resonant laser light in a magneto-optical trap and detected by observing its fluorescence. For the last 15 years, both the reliability and counting efficiency of the ATTA instrument have been steadily improved now making possible routine [81]Kr measurements in gas samples extracted from 100 to 200 l of groundwater or from 40 to 80 kg of ice.[23,24]

In principle, because the extreme sensitivity of the RIS-TOF technique coupled with the approach described in this work could allow study of sample 5 to 10 times smaller in size relative to ATTA but with a more complex process (three steps) as ATTA does not require isotopic enrichment step.

Instrumental development

General setup and isotope enrichment principle

The enrichment principle consists in implanting into Al foils simultaneously all Kr[+] ions separated using a magnetic mass spectrometer as shown in Fig. 1 for three isotopes [78]Kr, [83]Kr and [86]Kr. Then, Kr isotopes are selectively recovered by ablating the aluminum surface with an IR laser under high vacuum in a dedicated cell.

The instrument used for this development is a modified inductively coupled plasma-mass spectrometer ('Plasma Trace 2', Micromass, Wythenshawe, UK). A new ion source and a new Kr collecting chamber (see thereafter) have been both specially designed for our purpose.

The Plasma Trace 2 (PT2) initially had a double focusing sector field mass filter used in reverse Nier–Johnson geometry. Such geometry is well-suited for single mass or molecule detection with high resolution. For our aim of simultaneous multi-isotope implantations, the instrument was used with a conventional Nier–Johnson geometry. Consequently, the ion source is located in place of the
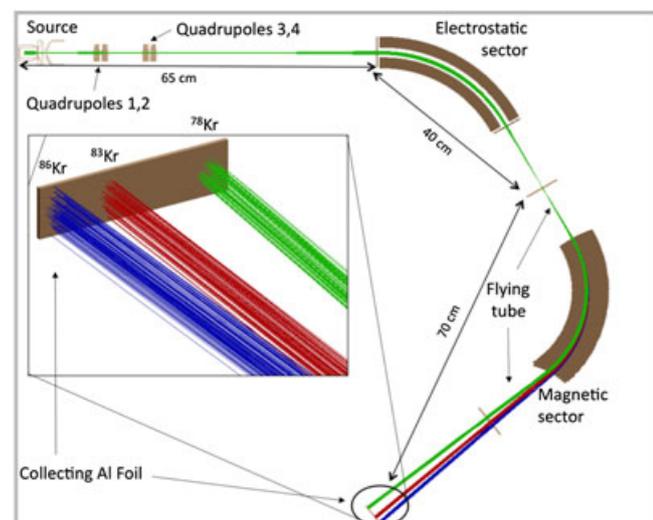
former ion detection arrangement, and the Al foils used for collecting the Kr isotopes is located in place of the former plasma ion source of the PT2.

A schematic of the mass spectrometer is presented in Fig. 2. The beam extracted from the ion source is focused using two doublets of electrostatic quadrupoles. The nearly collimated ion beam is focused after passing through the electrostatic analyzer (ESA) and before entering the magnetic sector. The measurement of the ion currents collected on a set of large slits (horizontal aperture 13 mm and vertical aperture 25 mm) located both at the entrance and at the exit of the ESA allows to optimize the tuning of the quadrupoles assuring a good centering of the beam. The position of the quadrupoles, the electrostatic sector and the magnetic sector have been determined using the SIMION 8.1[25] code in order to optimize beam transmission within the mass spectrometer while taking into account the characteristics of the ion source.

Three gas purification devices work continuously during the implantation runs to reduce the partial pressure because of internal degassing of chemically active species, a Ti sponge at 780 °C and two Al–Zr alloy SORB-AC at 450 °C from SAES Group.

Development of the ion source

The source must be designed for large krypton samples containing between 10^{16} and 10^{17} atoms that roughly corresponds to the expected concentrations in the volume of air or water samples to be investigated. High Kr[+] beam currents allow transferring Kr atoms into the Al foils within a reasonably time, typically 3 to 5 h per run.

We have developed a forced electron beam-induced arc discharge-type ion source working at low temperature (<1000 °C after thermal modeling) having the capability to operate at high pressure (up to 10^{-4} mbar) and to provide high extracted current (>0.5 μA) with good stability. The source design is described in
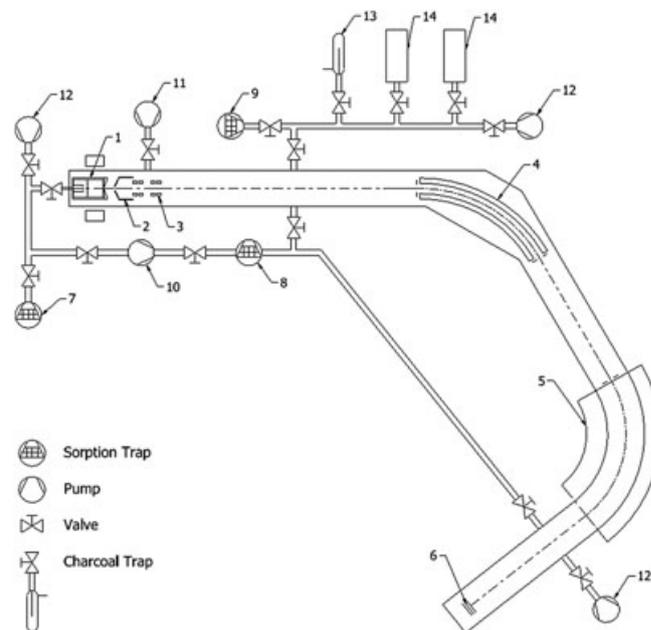

Figure 2. Schematic representation of the mass spectrometer: (1) ion source (refer details in Figure 3), (2) extractor lens, (3) quadruple doublets, (4) electrostatic sector, (5) magnetic sector, (6) collecting plates, (7) getter type SORB-AC CapaciTorr CF16 – MK2 from SAES Getter, (8) getter type SORB-AC GP50 from SAES Getter, (9) Ti sponge getter, (10) turbo-molecular pump, (11) ionic pump, (12) turbo-molecular pump, (13) activated charcoal and (14) Kr calibration standard.

Figure 1. Enrichment principle. Schematic view of calculated Kr beams in the instrument and implantation of [78,83,86]Kr[+] ion beams on an Al plate.

Fig. 3. It is mounted on an insulating flange cooled by temperature controlled (15 °C) water circulating in the outside metal casing. Ions are essentially produced by electron impacts generated by a 0.3-mm diameter W filament with an accelerating voltage of 65–85 V between the filament and a grid inside the source body, depending on the gas pressure in the source. Ions exit the source through a circular hole with a diameter of 1.6 mm and an exit aperture angle of 50°. The source body being at a voltage of 7000 V, ions are extracted, accelerated and focused by a grounded extraction lens. An angular divergence of the source of 19 mrad or 1.09° (half angle) has been measured allowing a good transmission of the beam inside the quadrupoles.

The mass spectrometer operates in static mode by isolating all pumping units. For increasing the efficiency of the ionization yield, neutral atoms of Kr are continuously recycled and injected inside the source body using a turbo molecular pump (Hi-Pace 80, Pfeiffer). This gas recirculation increases the ionization efficiency by a factor of 5 to 10 depending on the source tuning and allows maintaining a maximum pressure of ~10^{-6} mbar in the instrument. Before entering the turbo-molecular pump, the gas is exposed to a first Getter (type SORB-AC GP50 from SAES Getter). A second cleaning using a small getter (type SORB-AC CapaciTorr CF16 – MK2 from SAES Getter) completes purification of the gas. It is particularly efficient for trapping hydrogen molecules just before admitting into the source. It reduces significantly the production of hydrides inside the source and consequently the mass interferences at mass 81 ($^{80}Kr-H^+$) and at mass 85 ($^{84}Kr-H^+$).

Ion implantation process

Figure 4 presents a Kr spectrum measured by collecting Kr ion charges on a 0.25-mm wire mounted on a translator. The wire scans the Kr beam by a longitudinal translation perpendicularly to the beam direction on the image focus axis. The distance between two Kr peaks corresponding to a variation of one mass unit is 3.9 mm. The mass resolution at 10% valley is about 250.

A first Al foil is placed in front of the collecting foil holder (Fig. 5) at the focus points of the Kr isotope beams. This foil collects all major stable Kr^+ ions (*m/z* of ^{80}Kr, ^{82}Kr, ^{84}Kr and ^{86}Kr). A 4-mm slit and two 1.5-mm slits allow the implantation respectively of ^{78}Kr, ^{81}Kr and ^{85}Kr isotopes into a second underneath Al foil. At the end of the implantation, this second Al foil contains isotopically enriched ^{78}Kr, ^{81}Kr and ^{85}Kr with respect to the other Kr isotopes. The implantation of $^{78}Kr^+$ ions allows monitoring the implantation yields.
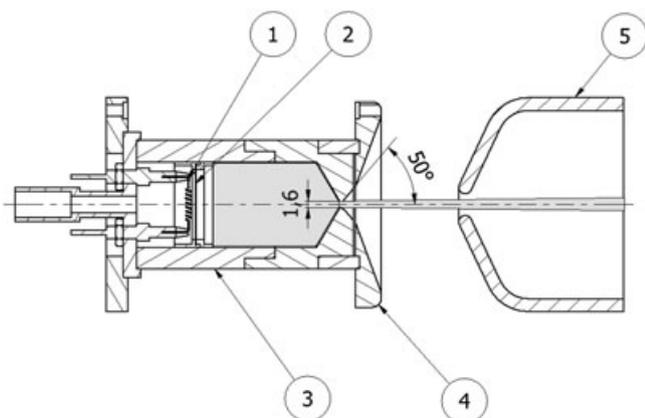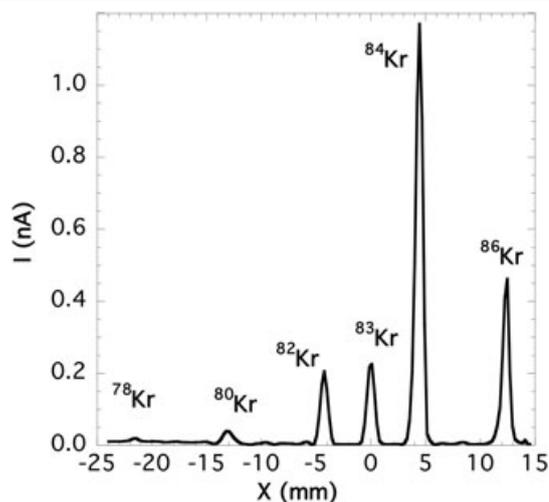

Figure 4. Kr spectrum obtained by collecting Kr ion charges on a 0.25-mm diameter wire with a longitudinal translation (step 0.25 mm) perpendicularly to the beam direction on the image focus axis.

The $^{83}Kr^+$ ion beam goes through two 1-mm slits opened on both foils to a Faraday cup for beam monitoring. The power supply of the magnetic sector is automatically adjusted every minute using a Labview interface in order to get the maximum ion current on the detector and to always implant each isotope beam all the time exactly at the same position on the foil.

Concentrations for the Kr isotopes are analyzed using a 60°–12 cm radius mass spectrometer (MM1200, VG). The two Al foils are analyzed separately. The Al foils are then introduced in a cell that is evacuated using turbo molecular pump and kept at least for one night at a temperature of 70 °C to improve degassing of an eventual surface contamination.

Figure 6 shows the calculated using SRIM (Stopping and Range of Ions in Matter)[26] ion range distribution of Kr^+ ions implanted in an Al target at 7000 V. The calculated mean ion range is 8.5 nm with a straggling of 2.7 nm. About 99% of the ions are stopped within the first 20 nm, and most of them reach a minimum depth of 2 nm. Krypton isotope losses during the cleaning process overnight have been measured, and they are lower than 0.5‰ per hour confirming as
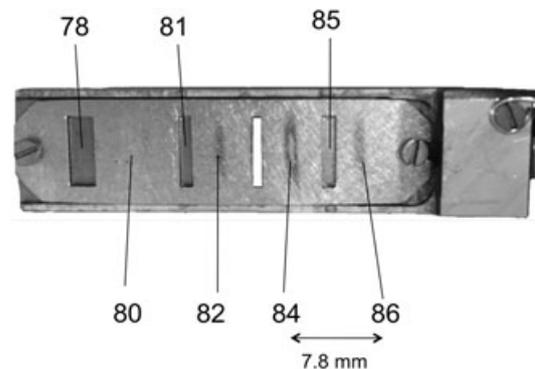

Figure 3. Schematic view of the ion source: (1) filament, (2) grid, (3) source cavity, (4) Wehnelt and (5) extractor.

Figure 5. The collecting Al foils on the holder. The Al foil above collects major isotopes $^{80,82,84,86}Kr$. Minor isotopes $^{78,81,85}Kr$ are implanted in a second foil through the slits. The $^{83}Kr^+$ ion bean goes through the plates and the support to a faraday cup to control the beam during the whole implantation process. Implantation marks on the foil are visible for ^{82}Kr, ^{84}Kr and ^{86}Kr reflecting the size and the shape of the beam.
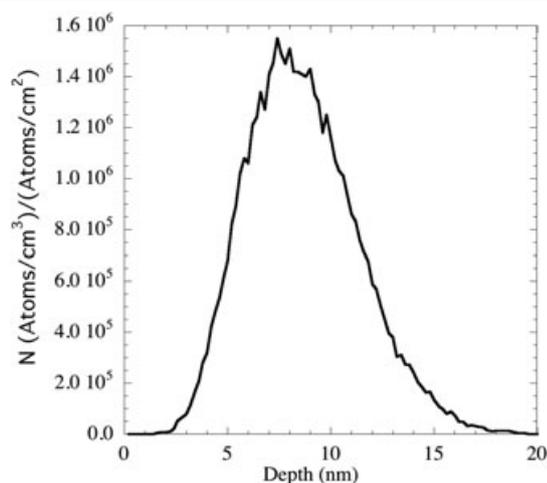
Figure 6. Calculated ion range distribution using SRIM of $^{84}Kr^+$ ions implanted in an Al target at 7000 V.

suggested by the calculation a good preservation of the atoms into the target after implantation.

Implanted ions are then separately released from the Al foils for further analyses by surface ablating process using a 50 mJ pulsed infrared laser beam and targeting the zones isotopically enriched with ^{81}Kr and ^{85}Kr. Laser-released krypton atoms are purified using hot Ti powder (750 °C) and SORB-AC cartridge pump from SAES Group. After purification, a small gas fraction (<1%) is introduced in the mass spectrometer to measure Kr isotopic ratios. A second small gas fraction is mixed with a ^{82}Kr-enriched spike to precisely determine atom numbers using isotope dilution method leading to relative uncertainties on absolute amounts of 2–3%. The atoms of $^{78,81,85}Kr$ left (>98%) are collected on an activated charcoal at liquid N_2 temperature in order to proceed to a second enrichment process before analyzing with the mass spectrometer dedicated to extremely high sensitivity measurements.[17] The second enrichment is currently performed using the mass spectrometer reported is this work.

Results and discussion

A typical result of an isotopic enrichment experiment is presented in Tables 1 and 2. The studied sample contains about 7×10^{15} Kr atoms with composition close to air. The initial current measured on the collecting plates was 509 nA (3.2×10^{12} ions/s) plus 30 nA (1.9×10^{11} ions/s) on the Faraday cup ($^{83}Kr^+$). This corresponds to a sensitivity of 2.5×10^{-2} A/torr. The experiment was stopped after 5 h and 40 min. The final current on the main plate was 124 nA (7.8×10^{11} ions/s) and 2.4 nA (1.5×10^{10} ions/s) on the detector for the $^{83}Kr^+$ ions.

Table 1. Implantation yields for ^{78}Kr expressed in unit of 10^{12} atoms and in % relative to the number of atoms initially introduced in the mass spectrometer

	^{78}Kr (10^{12} atoms)	%
Sample	21.7 ± 0.7	100%
After first enrichment	10.6 ± 0.4	(48.8 ± 2.4)%
After second enrichment	7.19 ± 0.3	(33.1 ± 1.7)%
All uncertainties are 2-σ errors.		

Table 1 reports the number of atoms for ^{78}Kr (expressed in 10^{12} atoms) first admitted in the mass spectrometer and collected on the Al foil respectively after the first and the second enrichment. The second column presents the corresponding percentages relative to the quantity of ^{78}Kr initially introduced in the mass spectrometer.

It shows that about 33% of the initial quantity of ^{78}Kr can be recovered after processing two implantation experiments.

Krypton isotope separation

As mentioned before, stable Kr isotopes are collected at the locations of the masses ^{81}Kr and ^{85}Kr because of the peak tailing effects. In order to evaluate the efficiency of the isotope separation, atom numbers implanted through the two 1.5-mm slits located at the m/z ratios of ^{81}Kr and ^{85}Kr are measured for all Kr isotopes.

Table 2 reports the number of atoms of $^{80,82,83,84,86}Kr$ isotopes initially introduced in the mass spectrometer as well as the implanted laser-released (at m/z of ^{81}Kr and ^{85}Kr) concentrations (in units of 10^{12} atoms) after the first and the second enrichment. Numbers in parenthesis refer for each isotope to the enrichment factors relative to the previous step.

The best enrichment factor (3500) is obtained for ^{83}Kr after the first enrichment. Krypton-83 has a mass difference of 2 relative to both ^{81}Kr and ^{85}Kr opposite to all other isotopes. Therefore, the interference because of the tailing effect is much lower. The enrichment factor of ^{80}Kr (1478) lies between the values observed for ^{82}Kr (2015) and ^{86}Kr (1309) suggesting a minimal contribution of the hydrides $^{80}Kr^+$-H at m/z = 81 and by extension of $^{84}Kr^+$-H at m/z = 85.

The enrichment factor for ^{84}Kr (767) appears significantly lower during the first enrichment. At the end of the first enrichment experiment, the residual gas in the mass spectrometer was analyzed. For all isotopes except ^{84}Kr, the percentages left relative to the initial Kr composition range from 6.8 to 9.0%. For ^{84}Kr, the percentage left reaches almost 40%. This clearly indicates an important saturation of the Al target, which leads to a limitation in the number of implanted atoms. In ^{84}Kr case, the implanted atom surface density roughly corresponds to 3×10^{16} atoms/cm². The measured quantity of implanted $^{84}Kr^+$ ions at the end of the experiment was 1.5×10^{15} atoms. Based on the implantation distribution given in Fig. 6, such a concentration roughly corresponds to 1 atom of Kr for 3 atoms of Al. It is probably the maximum possible concentration with our experimental configuration. As a consequence, the large excess in the instrument of ^{84}Kr relative to the other Kr isotopes increases significantly the probability of interference at the close mass m/z = 85 because of the tailing effect and could explain the lower enrichment factor.

During the second enrichment experiment with 767 times less ^{84}Kr atoms reintroduced, the saturation effect was not encountered. However, the enrichment factors range from 73 to 224, values 5 to 10 times lower than those obtained with the first enrichment run. This lower enrichment factors are because of an increase of the Kr concentration also by a factor of 5 to 10 inside the mass spectrometer because of a memory effect. This effect is generally associated to the release of Kr atoms implanted in metal parts during previous experiments performed with large quantities of gas as for the first enrichment run. Technique like the ion brushing is going to be investigated for reducing the memory effects. It consists in create high ion currents in the mass spectrometer using other chemical species like He or Ar. Krypton-implanted Kr^+ ions are then replaced by He or Ar ions in the contaminated metal parts lowering

Table 2. Kr isotopic concentrations and total Kr concentration of cumulated laser-released atoms at masses 81 and 85 after each implantation experiment in unit of 10^{12} atoms

	^{80}Kr	^{82}Kr	^{83}Kr	^{84}Kr	^{86}Kr	Total
	(Concentrations in unit of 10^{12} atoms)					
Admitted sample	136 ± 5	685 ± 27	658 ± 26	3250 ± 130	961 ± 38	$\mathbf{4909 \pm 245}$
After the first enrichment						
Quantity of atoms	0.092 ± 0.004	0.34 ± 0.014	0.188 ± 0.008	4.24 ± 0.17	0.734 ± 0.029	$\mathbf{5.41 \pm 0.27}$
(enrichment factor)	(1478)	(2015)	(3500)	(767)	(1309)	**(907)**
% of ^{x}Kr left in the MS	6.9%	8.9%	6.8%	39.7%	9.0%	**30.4%**
($x = 80, 82, 83, 84, 86$)						
After the second enrichment Quantity of atoms	0.00118 ± 0.00005	0.00463 ± 0.00018	0.00212 ± 0.00008	0.0189 ± 0.0008	0.00667 ± 0.00027	$\mathbf{0.0335 \pm 0.0017}$
(enrichment factor)	(78)	(73)	(87)	(224)	(110)	**(172)**
Final enrichment factor	$1.15\ 10^5$	$1.48\ 10^5$	$3.11\ 10^5$	$1.72\ 10^5$	$1.44\ 10^5$	$\mathbf{1.47\ 10^5}$

Enrichment factors are calculated relative to the quantity of atoms introduced at each step. Relative uncertainties on % Kr left in the MS and on enrichment factors are 5%. All uncertainties are 2-σ errors.

the memory signal level. A gain by a factor or 10 or 20 could be expected this way.

All in all, taking into account all Kr isotopes, the final enrichment factor is 1.47×10^5. The most limiting isotope is ^{84}Kr that represents 60% of the atoms left.

Conclusion

A double focusing sector field mass filter used in Nier–Johnson geometry has been built in order to perform Kr isotope enrichment for ^{81}Kr and ^{85}Kr isotopes. Krypton ions are accelerated at 7 keV and implanted in Al foils after separation using the magnetic sector. A specific ion source has been designed capable of generating high ion beams ($>0.5\ \mu A$) to transfer into the collecting Al foils significant fractions of large Kr samples (10^{15} to 10^{16} atoms) initially introduced in the instrument in 3 to 5 h. Implanted Kr isotopes can be further selectively released from the Al foil by local laser ablation. Two enrichment experiments have been successively applied to a Kr sample containing about 7×10^{15} atoms with isotopic composition close to air. The final enrichment yield is found to be 33%. Large excesses (30%) of ^{84}Kr in the residual gas left in the mass spectrometer after the first enrichment have been observed because of a saturation of the Al collecting foil. This excess leads to larger interferences of ^{84}Kr at the mass $m/z = 85$. The final enrichment factor taking into account stable ^{80,82,84,86}Kr isotope is found to be 1.47×10^5. Expected performances in terms of implantation yield and isotope separation have been globally reached. However, during the second enrichment run, the Kr memory of the instrument constitutes a clear limitation of enrichment factor by lowering it at least by a factor of 5 relative to the first enrichment experiment. Therefore, the next step will be the development of a second mass spectrometer dedicated exclusively to the second enrichment experiments. Other materials than Al may also be tried to improve ^{84}Kr implantation yield and therefore attenuate the mass interference.

References

[1] H. Oeschger. Accelerator mass spectrometry and ice core research. *Nucl. Instr. Meth.* **1987**, B29, 196–202.

[2] S. D. Kramer, G. S. Hurst, C. H. Chen, M. G. Payne, S. L. Allman, R. C. Phillips, B. E. Lehmann, H. Oeschger, H. H. Loosli, R. D. Willis, N. Thonnard. Analysis of ^{81}Kr in groundwater using laser resonance ionization spectroscopy. *Nucl. Instr. Meth.* **1986**, B17, 395–401.

[3] B. E. Lehmann, H. Oeschger, H. H. Loosli, G. S. Hurst, S. L. Allman, C. H. Chen, S. D. Kramer, M. G. Payne, R. C. Phillips, R. D. Willis, N. Thonnard. Counting ^{81}Kr atoms for analysis of groundwater. *J. Geophys. Res.* **1985**, 90, 11,547–11,551.

[4] B. E. Lehmann, H. H. Loosli, D. Rauber, N. Thonnard, R. D. Willis. ^{81}Kr and ^{85}Kr in groundwater, Milk River Aquifer, Alberta Canada. *Appl. Geochem.* **1991**, 6(4), 419–423.

[5] P. Collon, W. Kutschera, H. H. Loosli, B. E. Lehmann, R. Purtschert, A. Love, L. Sampson, D. Anthony, D. Cole, B. Davids, D. J. Morrissey, B. M. Sherrill, M. Steiner, R. C. Pardo, M. Paul. ^{81}Kr in the Great Artesian Basin, Australia: a new method for dating very old groundwater. *Earth Planet. Sci. Lett.* **2000**, 182, 103–113.

[6] N. C. Sturchio, X. Du, R. Purtschert, B. E. Lehmann, M. Sultan, L. J. Patterson, Z. -T. Lu, P. Müller, T. Bigler, K. Bailey, T. P. O'Connor, L. Young, R. Lorenzo, R. Becker, Z. El Alfy, B. El Kaliouby, Y. Dawood, A. M. A. Abdallah. One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. *Geophys. Res. Lett.* **2004**, 31: L05503 (1-4).

[7] N. C. Sturchio, K. L. Kuhlman, R. Yokochi, P. C. Probst, W. Jiang, Z. -T. Lu, P. Mueller, G. -M. Yang. Krypton-81 in groundwater of the Culebra Dolomite near the Waste Isolation Pilot Plant, New Mexico. *J. Contam. Hydrol.* **2014**, 160, 12–20.

[8] H. H. Loosli. A dating method with ^{39}Ar. *Earth Planet. Sci. Lett.* **1983**, 63, 51–62.

[9] C. Buizert, D. Baggenstos, W. Jiang, R. Purtschert, V. V. Petrenko, Z. -T. Lu, P. Müller, T. Kuhl, J. Lee, J. P. Severinghaus, E. J. Brook. Radiometric ^{81}Kr dating identifies 120,000-year-old ice at Taylor Glacier, Antarctica. *Proc. Natl. Acad. Sci. U. S. A.* **May 2014**, 111(19), 6876–6881.

[10] W. Smethie Jr., G. Mathieu. Measurement of Krypton-85 in the ocean. *Mar. Chem.* **1986**, 18, 17–33.

[11] W. M. Smethie Jr., H. G. Ostlund, H. H. Loosli. Ventilation of the deep Greenland and Norwegian seas: evidence from krypton-85, tritium, carbon-14 and argon-39. *Deep Sea Res.* **1986**, 33, 675–703.

[12] O. Connan, K. Smith, C. Organo, L. Solier, D. Maro, D. Hébert. Comparison of RIMPUFF, HYSPLIT, ADMS atmospheric dispersion model outputs, using emergency response procedures, with ^{85}Kr measurements made in the vicinity of nuclear reprocessing plant. *J. Environ. Radioact.* **2013**, 124, 266–277.

[13] W. H. Weiss, H. Sartorius, H. Stockburger. Global distribution of atmospheric ^{85}Kr. A database for the verification of transport and mixing models. *Isotopes of Noble Gases as Tracers in Environmental Studies*, (*Proc. Consultants Meeting*) IAEA, Vienna, **1992**, 29-62.

[14] O. Connan, L. Solier, D. Hébert, D. Maro, M. Lamotte, C. Voiseux, P. Laguionie, O. Cazimajou, S. Le Cavelier, C. Godinot, M. Morillon, L. Thomas, S. Percot. Near-field krypton-85 measurements in stable meteorological conditions around the AREVA NC La Hague reprocessing plant: estimation of atmospheric transfer coefficients. *J. Environ. Radioact.* **2014**, *137*, 142–149.

[15] G. Zuzel, H. Simgen, G. Heusser. Ar and Kr concentrations in nitrogen as a measure of the ^{39}Ar and ^{85}Kr activities in connection with the solar neutrino experiment Borexino. *Appl. Radiat. Isot.* **2004**, *61*, 197–201.

[16] H. Simgen, G. Heusser, G. Zuzel. Highly sensitive measurements of radioactive noble gas nuclides in the Borexino solar neutrino experiment. *Appl. Radiat. Isot.* **2004**, *61*, 213–217.

[17] E. Gilabert, B. Lavielle, B. Thomas, C. Moulin, S. Topin, F. Pointurier. Ultratrace analysis of krypton isotopes by resonant ionization spectroscopy-time of flight mass spectrometry (RIS-TOF). *J. Anal. At. Spectrom.* **2016**, *31*, 994–1001.

[18] P. Collon, W. Kutschera, Z.-T. Lu. Tracing noble gas radionuclides in the environment. *Ann. Rev. Nucl. Part. Sci.* **2004**, *54*, 39–67.

[19] B. E. Lehmann, D. F. Rauber, N. Thonnard, R. D. Willis. An isotope separator for small noble gas samples. *Nucl. Instrum. Methods Phys. Res.* **1987**, *B28*, 571–574.

[20] H. H. Loosli, R. Purtschert, Rare gases *in Isotopes in the water cycle: past, present and future of a developing science*. P. K. Aggarwal, J. R. Gat *and* K. F. O. Froehlich (*eds*) **2005**, 91–95.

[21] N. Momoshima, F. Inoue, S. Sugihara, J. Shimada, M. Taniguchi. An improved method for ^{85}Kr analysis by liquid scintillation counting and its application to atmospheric ^{85}Kr determination. *J. Environ. Radioact.* **2010**, *101*, 615–621.

[22] C. Y. Chen, Y. M. Li, K. Bailey, T. P. O'Connor, L. Young, Z. -T. Lu. Ultrasensitive isotope trace analyses with a magneto-optical trap. *Science* **1999**, *286*, 1139–1141.

[23] Z. -T. Lu, P. Schlosser, W. M. Smethie Jr., N. C. Sturchio, T. P. Fischer, B. M. Kennedy, R. Purtschert, J. P. Severinghaus, D. K. Solomon, T. Tanhua, R. Yokochi. Tracer applications of noble gas radionuclides in the geosciences. *Earth Sci. Rev.* **2014**, *138*, 196–214.

[24] G. -M. Yang, L. -Y. Tu, C. –. F. Cheng, X. –. Y. Zhang, S. –. M. Hu. Counting radio-krypton atoms with a laser. *Chin. J. Chem. Phys.* **2015**, *28*, 445–351.

[25] www.SIMION.com

[26] J. F. Ziegler, M. D. Ziegler, J. P. Biersack. SRIM—the stopping and range of ions in matter. *Nucl. Instrum. Methods B* **2010**, *268*(11-12), 1818–1823.

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