Ultra-Trace Analysis of Krypton-85

H. Daerr, University of Hamburg ZNF, Hamburg, Germany
M. Kalinowski, University of Hamburg ZNF, Hamburg, Germany
M. Kohler, University of Hamburg ZNF, Hamburg, Germany
P. Sahling, University of Hamburg ZNF, Hamburg, Germany

heiner.daerr@uni-hamburg.de

To strengthen the efficiency and effectiveness of nuclear safeguards for detecting undeclared nuclear material and activities we propose to use the radioactive krypton isotope Krypton-85 as a tracer for clandestine plutonium production.
The main idea is to detect inexplicable atmospheric Kr85 concentration using the novel technology atom trap trace analysis (ATTA) in order to detect an undeclared reprocessing facility.
The Additional Protocol (INFCIRC/540, 1997) establishes the possibility to take environmental samples. Krypton-85 has a combination of unique features which makes it an ideal tracer for plutonium separation activities anywhere in the world. It is always generated along with plutonium and 99.9% remains within the fuel cladding. Due to its half-life of 10.76 years, significant amounts of krypton-85 still remain in the spent fuel even after long cooling times. Krypton is not removed from the atmosphere by any processes like chemical reactions or wash-out. Furthermore, there are no other relevant sources of krypton-85 besides of reprocessing.
The novel technology of atom trap trace analysis (ATTA) has been demonstrated by the physics group at Argonne National Laboratory in 1999. This is an ultra-sensitive trace analysis technique able to detect single krypton atoms.

We are setting up an ATTA apparatus in our laboratory, which is designed to fulfill all requirements to detect clandestine plutonium production.

Our goal is to determine Krypton-85 concentration of one liter samples of atmospheric air with an analysis time of 3 hours. This sample volume reduction is a significant step, since one liter can be taken as a grab sample by sucking it directly into pre-evacuated bottles at atmospheric pressure.

The small samples size and the short analysis time of ATTA will make it possible to use krypton-85 as a tracer for clandestine plutonium production with routine operation.

1. Introduction

The Additional Protocol [1] establishes the possibility of collecting environmental samples (e.g. air, water, vegetation, soil, smears) to draw conclusions about the absence of undeclared nuclear material or nuclear activities, but so far only swipe samples within inspected facilities are implemented routinely.
The IAEA safeguards still do not make use of the whole potential of the Additional Protocol. Our proposed technique will make a contribution to overcome this limitation.
Taking air samples enables the detection of undeclared reprocessing by analyzing the krypton-85 concentration. Therefore an assessment of the expected krypton-85 concentration at the sample location is needed. A global assessment of the krypton-85 concentration was done in [2]. In case a measured concentration is higher than the expected value, an unknown, additional source (e.g. undeclared reprocessing facility for clandestine plutonium production) was not included in the assessment and contributes to the local atmospheric krypton-85 concentration.
The global atmospheric krypton inventory is constantly increasing since the early 1950's. Due to strong point sources (e.g. La Hague) it has a high variability in time and space in the vicinity of these sources. Far from these sources (e.g. southern hemisphere) the variability at small time scales almost drops to zero and a constant, annual increase is noticeable. An undeclared reprocessing facility has to be detected against this varying background leading to a space and time depending detectability of an unknown source. On average the krypton-

85 concentration is about 1.6 Bq/m³.
There are several case studies showing the capability of krypton-85 for remote detection of reprocessing facilities [3, 4, 5, 6] underlining the feasibility of this approach. In [2] it was also demonstrated that detection of a reprocessing campaign up to 48 hours after the release is possible in most of the cases.

2. Requirements of a measurement technique for routine operation

A measurement technique should meet the following requirements.

Small and assessable errors
Every measurement is subject to systematic and random errors. These errors should be minimized and the residual inaccuracy assessable to make unquestionable and reliable statements. The errors are affected by the selectivity and the sensitivity of a technique.

Short measurement time
A short measurement time assures a prompt analysis when needed and the capability of analyzing many samples in a short time period, which is important in the case of routine sampling. The measurement time depends on the efficiency of a technique.

Small sample size
The possibility of analyzing small samples enables the collection of many samples in short time periods without the need of additional means (e.g. electricity). The sample size is determined by the efficiency of a technique.

Nondestructive method
A non-destructive technique allows the reuse of an analyzed sample by different methods or other apparatuses in order to confirm a certain result and increase credibility.

3. Measurement technique: Atom Trap Trace Analysis (ATTA)

The detection of individual krypton-atoms present in an atmospheric krypton gas sample with isotopic abundances in the range of 10^(-11) can only be accomplished by three methods:

Low level counting (LLC)
Low level counting (LLC) measures the radioactivity (β-particles and x-rays) of the tracer. This technique is applicable, if a sample can be analyzed in reasonably short measurement time. In order to achieve this a minimum activity of the tracer in stock is needed. The smallest sample size directly depends on the radioactive half-life of the specific tracer and on the available measurement period. Isotopes with a short radioactive half-life are thus preferred.

Accelerator mass spectrometry (AMS)
Accelerator mass spectrometry (AMS) is another method for counting atoms and is in contrast to LLC not restricted to radioactive tracers. The discrimination of atoms is achieved by employing different ratios of q/m of isotopes with q being the electric charge and m the mass of the ion. The main technical challenge of this method is the separation of the isotope of interest from its isobaric background (e.g. Kr-81and Br-81, Kr-85 and Rb-85). For isobaric separation high energies are needed which require large and expensive accelerator facilities impeding a wide use of AMS since such large facilities (primarily devoted to nuclear physics) are typically not available for routine measurements of large sample numbers [7].

Atom Trap Trace Analysis (ATTA)
A new method for ultra rare trace analysis referred to as atom trap trace analysis (ATTA) became possible due to dramatic advances in the field of laser cooling and laser manipulation of atoms towards the end of the 1980s. A group at the Argonne National Laboratory performed the first proof-of-principle experiment for single atom trapping of rare gas atoms in 1999 [8]. The high isotopic selectivity of laser cooling and trapping methods promise to make ATTA superior to the before mentioned methods. The isotope shift of atomic energy levels (typical a few GHz) can be easier used to distinguish and count different isotopes than separation relying on the charge to mass ratio.

A detailed discussion and comparison of LLC, AMS and ATTA is documented in [7]. ATTA can be applied to all atoms which can be laser cooled and trapped within a magneto-optical trap (MOT) including krypton-85 and krypton-81.

3.1 Basic concept of magneto-optical trap (MOT)

ATTA is an atom counting method. The atoms are counted individually by trapping and detecting them in a magneto-optical trap (MOT). A MOT is a widely used neutral atom trap for atomic physics experiments all over the world. In general a trap spatially confines a particle by a force that is only zero at the trap centre and non zero around the centre with a direction pointing towards the trap centre. A particle at a distance to the trap centre gets driven towards the trap centre. A magneto-optical trap spatially confines neutral atoms by the use of three pairs of counter propagating laser beams in all three directions crossing at one point (trap) in combination with an inhomogeneous magnetic field (see figure 1).

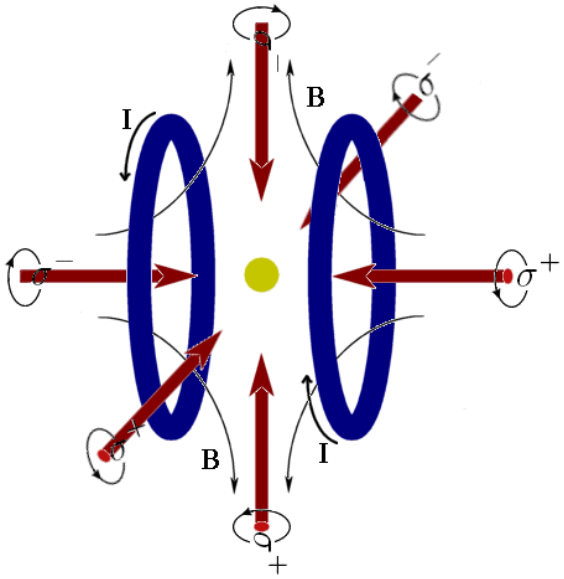

Figure 1: Sketch of a magneto-optical trap. In blue the two current coils generating the required magnetic field B denoted by the black arrows . The six laser beams are coloured in red. The trap centre is illustrated by the yellow point.

The absolute value of the magnetic field has a zero crossing at the trap centre and a constant increase in all three directions. The magnetic field manipulates the internal energy levels of the atoms space dependent. The mode of operation of a MOT can be explained in a one dimensional model (see figure 2).

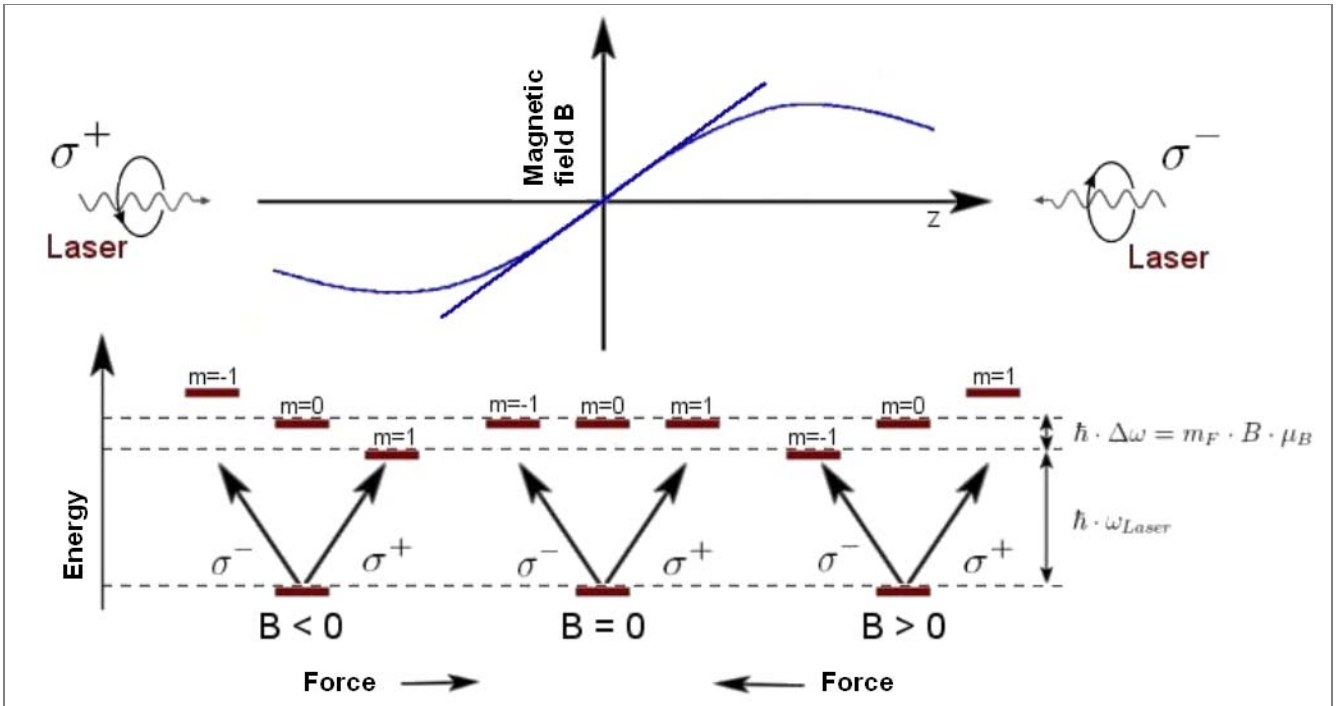

Figure 2: The mode of operation of a MOT is explained in a one dimensional model. The upper part shows the two counter-propagating laser beams and the linear magnetic field B (blue line). The lower part shows the space dependent splitting of the atomic magnetic sub-levels due to the magnetic field. An atom located at the left side is pushed to the right side towards the trap centre as it absorbs more photons from the laser beam coming from the left.

The upper part of the picture shows one of the three pairs of counter-propagating laser beams and the space dependent magnetic field. In the lower part the atomic energy levels and their space dependent changes due to the Zeeman-effect are shown. The laser light irradiated from the left side is counter clockwise (σ+) and the light from the right is clockwise (σ-) circular polarized. The σ+ (σ-) light drives the transition from the ground state to the m = 1 (m = -1) state. An atom located at the right side mainly absorbs photons from the σ+ light coming from the left and is therefore pushed to the trap centre. An absorbed photon from the laser light transfers energy but also momentum to the atom. The momentum is vectored in the direction of propagation of the laser light. When the atom decays spontaneously the direction of the photon is random and the momentum of the atom is changed again. But on average there is no momentum transfer due to the decay but a directed one due to the absorption. Kinetic energy is removed from the atom and it continuously scatters photons.
The scattered photons are used to detect a trapped atom. Many million photons per second are spontaneously emitted from one atom. Therefore a MOT is highly selective, as trapping requires many absorbed photons with the right frequency matching the frequency of the transition. A 'wrong' atom might also scatter a few photons, but never millions per second needed for trapping.
In principle about 10^8 -10^9 atoms can be trapped simultaneously in a MOT. The lifetimes of a trapped atom is limited to 1s - 10s due to collisions with residual background atoms and an imperfect cooling cycle. A MOT can only operate in ultra high vacuum environment (p < 10^(-9) mbar).
A MOT can only trap slow atoms with a velocity of less than 30 m/s – 50 m/s. For efficient trapping the atoms of interest have to be slowed down before entering the capture volume of the MOT.

3.2 Trace analysis of krypton-85 using a magneto-optical trap

Krypton-85 is so rare that only single atoms get trapped in a MOT and detected by their fluorescence. As krypton is a noble gas, its first excited state has an energy corresponding to a vacuum ultra violet (VUV) photon with a wavelength of 123.6 nm. However, no laser radiating at a wavelength of 123.6 nm is available. To manipulate krypton atoms with lasers, they need to be excited to a metastable state serving as the ground state for laser cooling. The metastable state has a lifetime τ of about 40 s [9] sufficiently long for trapping and detecting. Krypton has an almost closed two level system suitable for laser cooling including the metastable state as ground state. The required wavelength of 811.5 nm is easily accessible using diode lasers.

The efficiency of an ATTA experiment is a product of the following single, partly interdependent efficiencies:

a. Efficiency of metastable state production
b. Efficiency of transversal and longitudinal cooling of atoms for capturing in the MOT
c. Capture and trapping efficiency of the MOT
d. Detection efficiency of a trapped atom

The challenge is to implement a design that maximizes these single efficiencies.
The bottle neck of ATTA with krypton is the production of the metastable state. In principle there are two ways of excitation. Excitation using electron atom collisions and optical excitation. The scheme first mentioned is realized by a DC or RF discharge [10]. The second one will be realized in experiment presented here and can be accomplished by using a krypton plasma lamp providing incoherent VUV photons at 123.6 nm and an IR- laser at 819 nm (see figure 3).

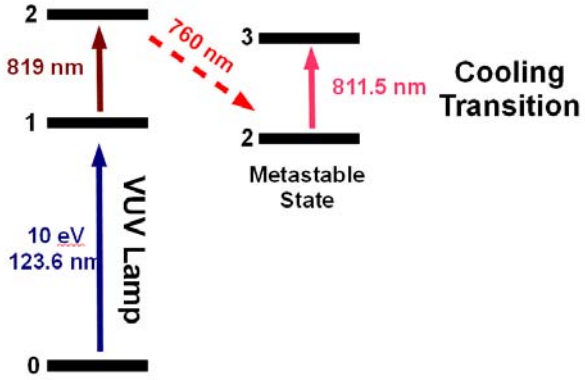

Figure 3: The relevant energy levels (black lines) without hyperfine splitting for the optical excitation are illustrated. For the production of metastable krypton atoms a VUV photon at 123.6 nm is required to excite the atom to the first excited state. Another infrared photon at 819 pumps the atom to a state from which the spontaneous decay to the metastable state occurs with a probability of about 75 %.

The VUV and the IR photons excite the atoms to a state from which it spontaneously decays (760 nm) to the metastable state with a high probability of about 75 %.

The excitation using a discharge needs a certain pressure at the location of the discharge to maintain it. This results in a lower limit for the number of krypton atoms and therefore the sample size. This can be circumvented by adding other noble gases e.g. commercially available argon, as it is free of krypton contamination. But still a certain number of atoms in the apparatus are required and the sample gets contaminated with argon.
The ATTA setup for krypton first realized in [8] (see figure 4) consists of a RF discharge excitation line followed by a transversal cooling stage, creating an excited atom beam with a reduced beam angle spread. The beam enters a Zeeman slower which is able to slow down about 80 % of the atoms below 30 m/s, which is followed by the MOT.

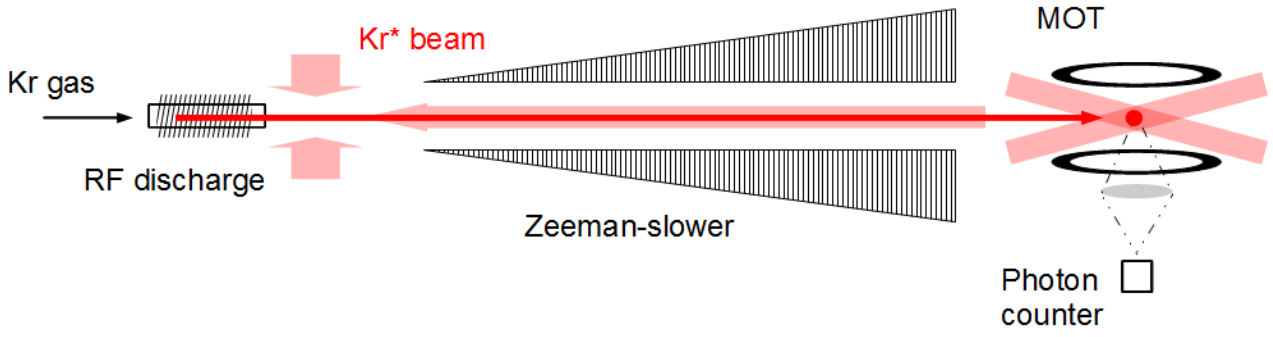

Figure 4: The setup used in other ATTA experiments is illustrated in this figure. A thermal atom beam is excited to the metastable state by a RF discharge. A transversally cooling stage reduces the angle spread of the beam before it enters the Zeeman-slower slowing the atoms below the capture velocity of the MOT.
The atoms are trapped in the MOT and detected using the scattered photons, which result from trapping.

This kind of set up has some disadvantages:

- The RF excitation limits the sample size or requires addition of other gases.

- Due to the relative high pressure at the location of the RF excitation, the mean free path of the atoms is relatively short allowing for collisions de-exciting of a large fraction of the metastable atoms [12].
- The laser for Zeeman-slower propagates through the MOT and produces additional stray light.
- There is a high non-metastable atom flux in the detection chamber reducing the trapping and therefore the detection time.
- The slowed atoms are again transversally heated by the Zeeman-slower lowering the MOT capture efficiency.

To overcome these limitations a trapping and detection mode is implemented witch doubles the measurement time. To sum up the advantages of the setup not followed in the present experiment a Zeeman-Slower slows about 80 % of atoms (below 30 m/s) and a high atom flux is created. The efficiency of the RF excitation efficiency is as high as of the optical excitation and the proof of principle that this setup is capable to determine atmospheric krypton-85 to krypton-81 ratio was given [13].
Our design includes the optical excitation in a way that the required sample size is greatly reduced without adding other gases.
In the presented experiment a two dimensional MOT (2D-MOT) [13] with integrated optical excitation is used for the production of a slow and collimated atom beam. The combination of 2D-MOT and 3D-MOT works as well as the combination of a Zeeman-slower and a 3D-MOT.
The advantages of using a 2D-MOT instead of a Zeeman-slower are improved capturing and detection conditions. A 2D-MOT produces an isotope selected cold atom beam with a longitudinal (8 ± 3.3 m/s) and transversal (< 0.2 m/s, $T < 300$ μK) velocity distribution ideal for capturing the atoms in the 3D-MOT. Due to these small transversal velocities a differential pumping stage with small passage of thermal atoms can be implemented resulting in a better vacuum in the 3D-MOT chamber extending the trapping time and thus the detection time. As already mentioned, the produced atom beam has a small angle of spread, what increases the capture efficiency. Therefore we will be able to implement single mode operation with continuous detection and trapping, cutting the measurement time in half.
Additionally, we plan to trap and detect both krypton-81 and krypton-85 simultaneously, what again halves the measurement time.
The optical excitation will be implemented in the vacuum chamber of the 2D-MOT (see figure 5).

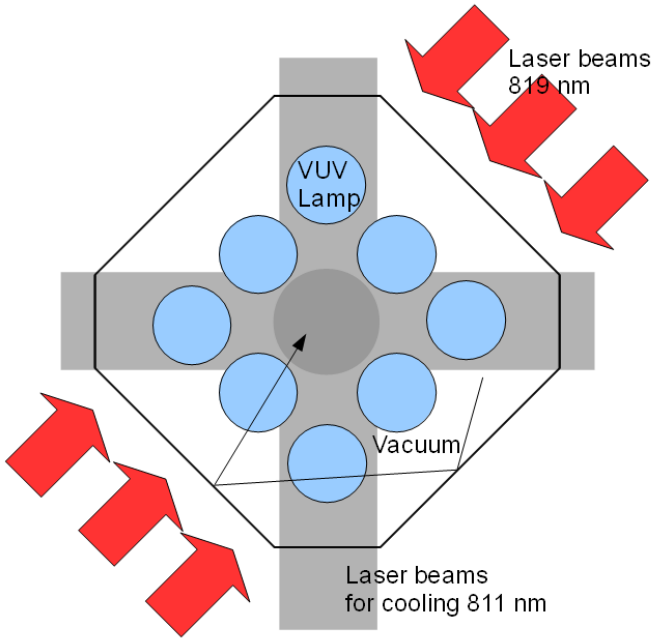

Figure 5: A lateral cut of the 2D-MOT with optical excitation is illustrated. The trapping laser beams are shown in light grey. The capture volume is illustrated in dark grey. The regions illuminated by the VUV lamp are indicated by the blue circles. A possible path of an atom is indicated by the black arrow. The atom collides with two walls, enters an optical excitation area and is trapped by the 2D-MOT and will be transferred to the 3D-MOT.

A lateral cut of the 2D-MOT with optical excitation is illustrated. A possible path of an atom is indicated by the arrow. The atom undergoes two wall collisions, enters an optical excitation area and then is tapped by the 2D-

MOT. With every collision atoms change their velocities and directions. Thus krypton atoms have a low but non-zero probability, that their velocities change below the capture velocity (v < 30-50 m/s) of the 2D-MOT. In case a slow krypton-85 atom has the right direction to enter an optical excitation area, it might get excited and then captured by the 2D-MOT. It will be transferred with a high probability into the 3D-MOT and detected. A slow atom needs a longer time to travel through the optical excitation area than a fast atom. As the excitation probability increases with time, slow atoms are more likely to get excited than fast atoms.
This setup strongly depends on the volumes of the excitation areas and the 2D-MOT as well as their distance. A small distance increases the probability that an atom leaving an excitation area enters the 2D-MOT capture volume. Therefore we positioned the VUV lamps as close as possibly to the 2D-MOT and enlarged the 2D-MOT volume by a factor four in comparison to common 2D-MOT – 3D-MOT setups.
The future apparatus consists of an ultra high vacuum system and a laser system providing the light for cooling and trapping of krypton atoms. The vacuum system has three separated chambers (see figure 6). The reservoir holds the bulk of the sample. It is connected to the 2D-MOT chamber by a gas dosing valve to control the krypton pressure in the 2D-MOT chamber. The 2D-MOT chamber is connected to the 3D-MOT chamber by a differential pumping stage to ensure ultra high vacuum conditions in the 3D-MOT chambers. All three chambers are connected by turbo molecular pumps to circulate the krypton gas within the apparatus. The circulation increases the efficiency by a factor of 1000 [14].

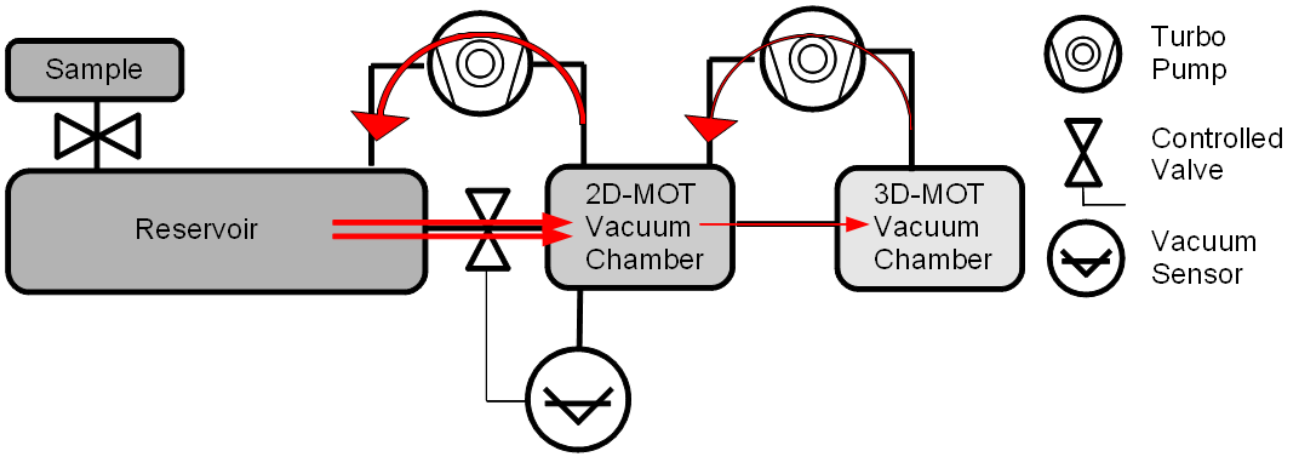

Figure 6: The picture shows the vacuum system of the presented ATTA experiment. The sample is connected to the reservoir chamber via a valve. Both sample and reservoir containing the bulk of the sample. A controlled leak valve is use to inlet the krypton gas into the 2D-MOT chamber. A turbo molecular pump is used to circulate the gas. The 2D-MOT chamber is connected to the 3D-MOT chamber using a differential pumping stage. A second turbo molecular pump transports the gas to the 2D-MOT chamber.

Error estimation
The krypton-85 concentration *C85* of an atmospheric sample is derived from the ratio R of the number of counted krypton-85 and krypton-81 atoms in a certain time period, *N85* and *N81*, respectively. Krypton-81 has a constant atmospheric concentration. It is exclusively generated by cosmic radiation and has a half life of about 230.000 years. Its secular equilibrium abundance is krypton-81/krypton = (5.2 ± 0.4) 10^(-13). At present this value has still an error of about 10 % limiting the determination of the krypton-85 to that accuracy at least. Another source of error is the determination of the ratio $R = N85/N81$. Trapping rare isotopes can be considered a stochastically independent random process. A trapped atom is not affected by another trapped atom in the case of small atom numbers. It can be shown, that the standard deviation ΔR of R is given by

$$\Delta R = \frac{R}{\sqrt{N81}}$$

with a relative error of

$$\frac{\Delta R}{R} = \frac{1}{\sqrt{N81}}.$$

Thus counting 100 krypton-81 ($N81 = 100$) leads to a relative error of 10 %.

Measurement time
Limiting the measurement time to 3 hours one krypton-81 atoms has to be counted roughly every two minutes on average. Achieving this count rate is challenging but feasible. In [14] a count rate of 240 krypton-81 atoms in

20 h was published, giving an averaged count rate of one krypton-81 atom every 5 minutes.
A combined trapping and detection mode will quicken the measurement with a factor of two. A higher net efficiency of the presented apparatus will further decrease the measuring time.

Sample size
This setup does not need a certain number of atoms to operate. But there is a pressure at which a 2D-MOT source works most efficient. It is the range of 10^(-8) mbar up to 10^(-7) mbar corresponding to a krypton atom number of about 10^(5) smaller than in air at atmospheric pressure. The efficiency of the apparatus is affected in case the number of krypton atoms is to low to maintain the optimal pressure in the 2D-MOT. Tiny sample sizes of a few ten ml air contain enough krypton for measurement.

Non destructive method
ATTA is an atom counting method that is not destructive. A measured sample can be extracted out of the apparatus. In this experiment a recovery of a measured sample is provided for reuse by different techniques or other apparatuses in order to confirm a certain result and increase credibility.

4. Status

The required laser system for cooling and trapping as well as for the optical excitation is almost finished. A self-made design of the VUV lamps has been developed and characterized. The vacuum components are manufactured in the mechanical work shop, at the moment. We intend to finish the assembling within the next year.

5. Conclusion

The presented ATTA experiment is designed to fulfil the requirement for analyzing small sized atmospheric samples. The key ingredient is the use of a 2D-MOT, which will make it possible to reduce the measurement time by a factor of 4 and to integrate the optical excitation in an efficient way. The aim is to analyze atmospheric samples with a volume of one litre of air within 3 hours.

6. Acknowledgement

We would like to thank the Quantum Gases and Spectroscopy Group of Prof. Sengstock (Insitut für Laserphysik, University of Hamburg) for the technological cooperation.
We thank the Deutsche Stiftung Friedensforschung (DSF) and the Deutsche Forschungsgemeinschaft (DFG) for financial support.

[1] INFCIRC/540, 1997, www.iaea.org/Publications/Documents/Infcircs/1997/infcirc540c.pdf
[2] J. O. Ross, Phdthesis, *Simulation of atmospheric krypton-85 transport to assess the detectability of clandestine nuclear reprocessing*, Carl Friedrich von Weiszäcker-Centre for Science and Peace Research of the University of Hamburg (2010)
[3] Kalinowski, M. B.; Sartorius, H.; Uhl, S. & Weiss, W.
Conclusions on plutonium separation from atmospheric krypton-85 measured at various distances from the Karlsruhe reprocessing plant Journal of Environmental Radioactivity, **2004**, *73*, 203 - 222
[4] Kemp, R. & Schlosser, C.
Erratum to performance estimate for the detection of undeclared nuclear-fuel reprocessing by atmospheric 85Kr [J. Environ. Radioact. 99 (2008) 1341-1348]
Journal of Environmental Radioactivity, **2009**, *100*, 99 - 99

[5] Goodman, M. S.
Spying on the Nuclear Bear
Anglo-American Intelligence and the Soviet Bomb
Stanford University Press, **2007**
[6] F. von Hippel and D.H. Albright, *Quantities of fissile materials in U.S. and Soviet nuclear weapons arsenals*, *PU/CEES Rep. No. 168*, Princeton University, Center for Energy and Environmental Studies, Princeton, N.Y (1986).
[7] Collon, P.; Kutschera, W. & Lu, Z.-T.
TRACING NOBLE GAS RADIONUCLIDES IN THE ENVIRONMENT
Annual Review of Nuclear and Particle Science, **2004**, *54*, 39-67
[8] Chen, C. Y.; Li, Y. M.; Bailey, K.; O'Connor, T. P.; Young, L. & Lu, Z.-T.
Ultrasensitive Isotope Trace Analyses with a Magneto-Optical Trap
Science, **1999**, *286*, 1139-1141
[9] Katori, H. & Shimizu, F.
Lifetime measurement of the 1s5 metastable state of argon and krypton with a magneto-optical trap
Phys. Rev. Lett., American Physical Society, **1993**, *70*, 3545-3548
[10] Chen, C. Y.; Bailey, K.; Li, Y. M.; O'Connor, T. P.; Lu, Z.-T.; Du, X.; Young, L. & Winkler, G.
Beam of metastable krypton atoms extracted from a rf-driven discharge
Review of Scientific Instruments, AIP, **2001**, *72*, 271-272
[11] Welte, J.; Ritterbusch, F.; Steinke, I.; Henrich, M.; Aeschbach-Hertig, W. & Oberthaler, M. K.
Towards the realization of atom trap trace analysis for 39 Ar
New Journal of Physics, **2010**, *12*, 065031
[12] Dieckmann, K.; Spreeuw, R. J. C.; Weidemüller, M. & Walraven, J. T. M.
Two-dimensional magneto-optical trap as a source of slow atoms
Phys. Rev. A, American Physical Society, **1998**, *58*, 3891-3895
[13] Du, X.; Bailey, K.; Lu, Z.-T.; Mueller, P.; O'Connor, T. P. & Young, L.
An atom trap system for practical [sup 81]Kr dating
Review of Scientific Instruments, AIP, **2004**, *75*, 3224-3232