Purification of N_2 and Ar

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Outline

- Requirements
- Gas purification by adsorption
- N_2 purification
- Ar purification
- Techniques for analysis
- Summary

Production

- N_2, Ar are produced from air by rectification
- Traces of atmospheric noble gases remain in final product
- Final purity depends on individual plant

Radioactive noble gas nuclides in the air

	Sources	Activity concentration (STP)
^{42}Ar	cosmogenic	0.5 μBq/m³ air 50 μBq/m³ Ar
^{39}Ar	cosmogenic	17 mBq/m³ air 1.8 Bq/m³ Ar
^{85}Kr	^{235}U fission (nuclear fuel reprocessing plants)	1.4 Bq/m³ air 1.2 MBq/m³ Kr
^{222}Rn	Primordial ^{238}U	10 to >100 Bq/m³ air

Requirements

- ^{222}Rn:
  - MC simulations [Baudis 2002]:
  - 0.5 μBq/m³ N_2 (STP) = $6 \cdot 10^{-5}$ events/(kg·y·keV)

BOREXINO has achieved this goal

- ^{42}Ar:
  - MC simulations [Schönert]:
  - 50 μBq/m³ N_2 (STP) = $4 \cdot 10^{-5}$ events/(kg·y·keV)

^{42}Ar naturally low enough

Requirements

- Q-value of ^{39}Ar and ^{85}Kr below 700 keV:
- But dead-time problem when Ar scintillation is used (slow decay time: 1 μs)
- Assume 30 m^3 active volume
  - ^{39}Ar rate: 50 kHz **OK!**
  - ^{85}Kr rate not higher $\Rightarrow$ **≤1 ppm krypton** required

Gas purification by adsorption

- Applied when highest purities are required
- Based on different binding energies
- Pore size distribution is crucial
- Activated carbon suited for most applications

Henrys Law

$$n = H \cdot p$$

- n = number of moles adsorbed [mol/kg]
- p = partial pressure of Kr [Pa]
- H = Henry coefficient [mol/(kg·Pa)]

- valid for low partial pressures

Single component adsorption model for H

- S. Maurer, Ph.D. thesis, TU München (2000)
  - Adsorption on activated carbon
  - based on van-der-Waals equation
- simple empirical formula derived:

$$H\left[\frac{\mathrm{mol}}{\mathrm{kg}\cdot\mathrm{Pa}}\right]=\exp\left\{\left(-0.05+\frac{81}{T[\mathrm{K}]}\right)\cdot\frac{T_C[\mathrm{K}]}{\sqrt{P_C[\mathrm{bar}]}}-17.5\right\}$$

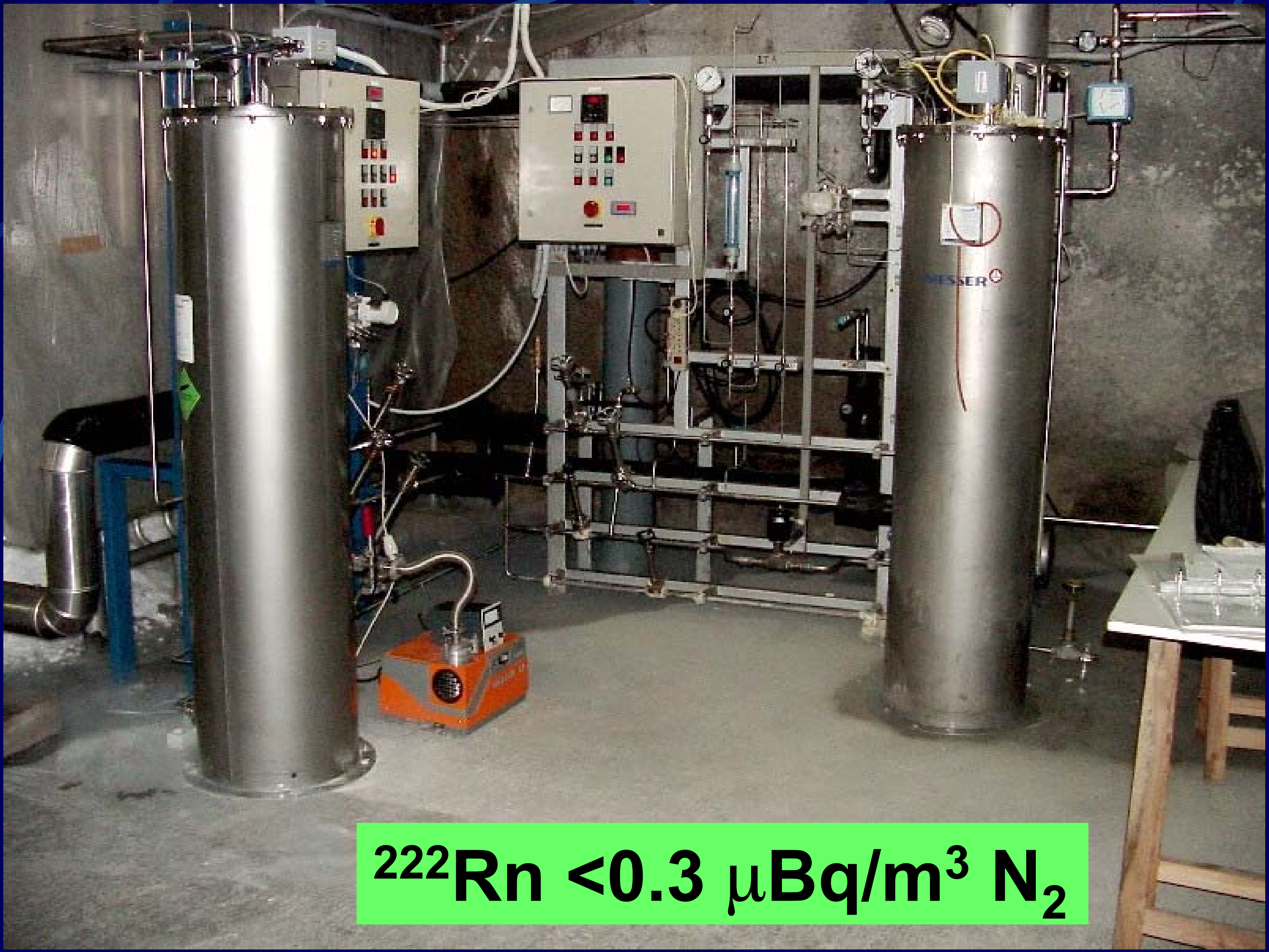
Single component adsorption model for H

Gas	T_C [K]	P_C [bar]	$T_C \cdot P_C^{-0.5}$ [$K \cdot bar^{-0.5}$]	H [mol/(kg·Pa)] @ 77 Kelvin
Ar	151	49	21.6	2E+2
N_2	126	34	21.6	2E+2
Kr	209	55	28.2	2E+5
Rn	377	63	47.6	1E+14

N_2 purification

- Lots of know-how at MPI-K (BOREXINO)
- Removal of Ar not possible by adsorption
- Rn purification possible but problem with ^{222}Rn emanation
- Highly pure synthetic carbon „Carbo Act“ ^{222}Rn emanation <0.3 mBq/kg

N_2 purification

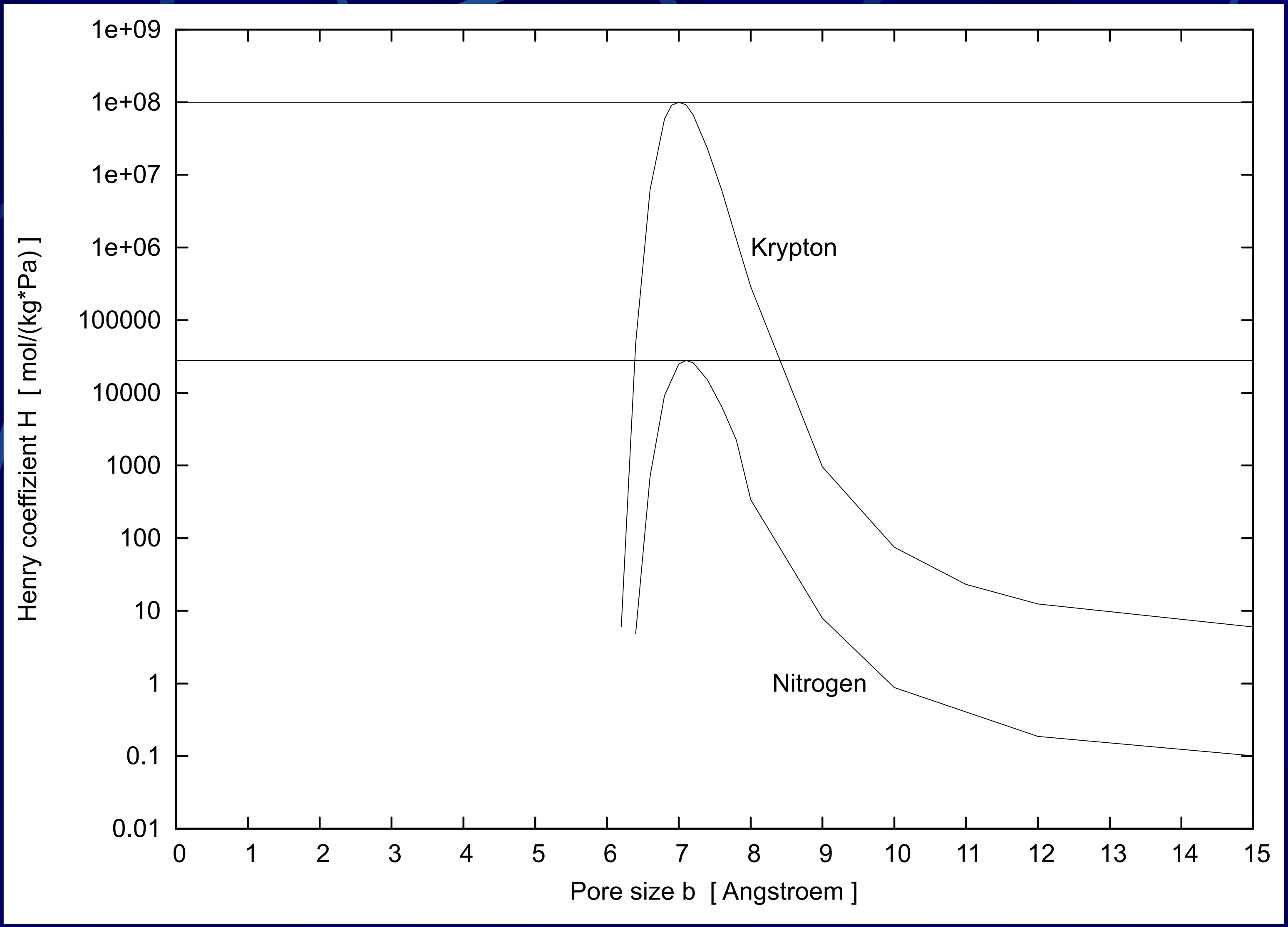


^{222}Rn <0.3 μBq/m^3 N_2

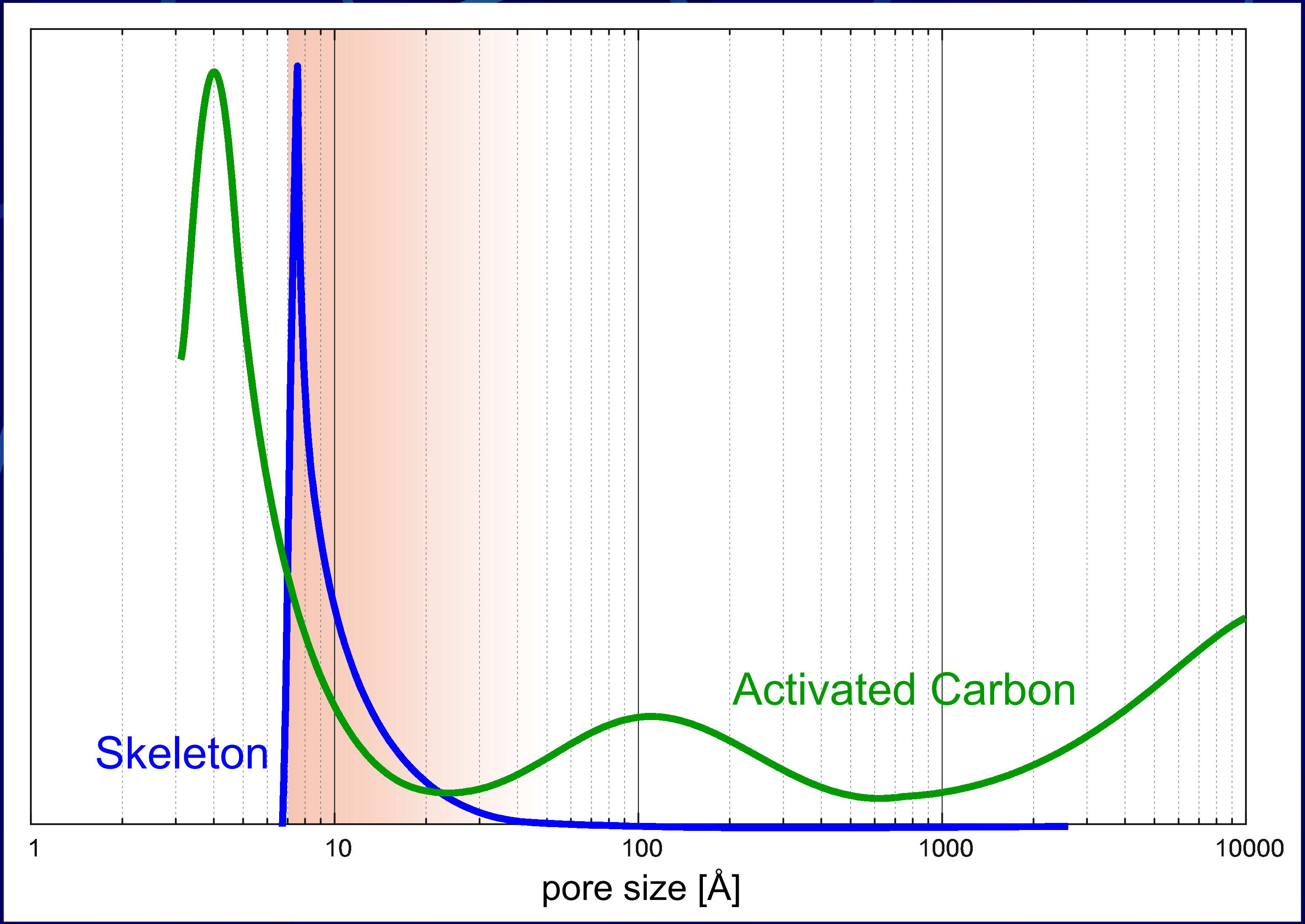
Purification of N_2 from Kr

- Single component adsorption model fails for binary system N_2/Kr
- „Competition“ between N_2 and Kr for available adsorption sites
- Henry coefficient for Kr adsorption drops from $\sim 10^2$ to $\sim 10^{-4}$ when N_2 is present

H and pore sizes



Pore size distributions



Purification of N_2 from Kr

- Further improvment by gas phase adsorption at low temperatures
- Pores and gas phase lead to H ~1 mol/kg/Pa
- More than 500 m^3 of N_2 (STP) can be purified with ~1 kg of adsorber (V=H·R·T·m)

Purification of N_2
- Summary -

- Rn removal no problem
- Ar removal impossible
- Kr removal technically feasible but requires
  - low temperature gas phase adsorption
  - Pore size-tuned carbon adsorbers

Single component adsorption model for H

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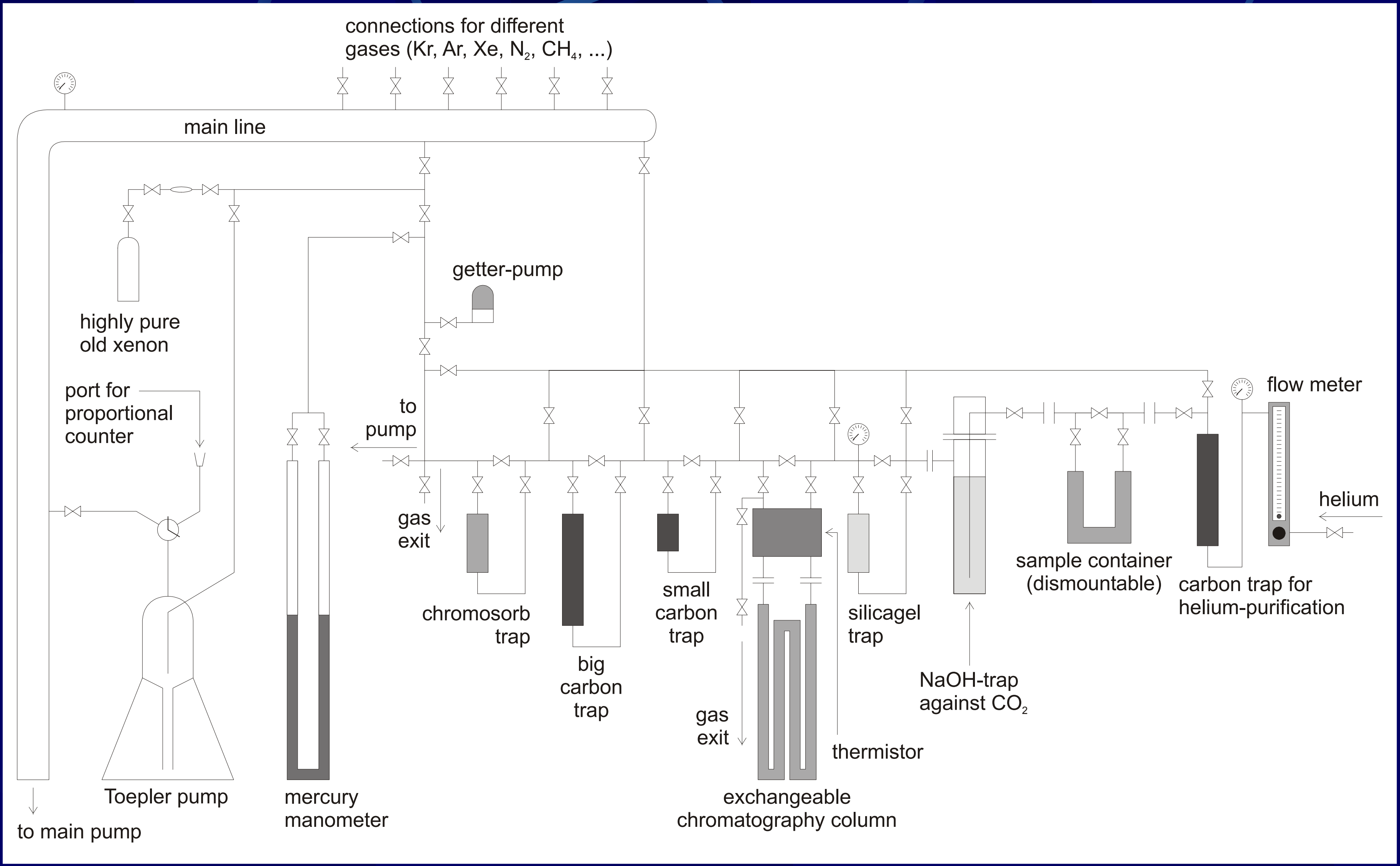
Purification of Ar

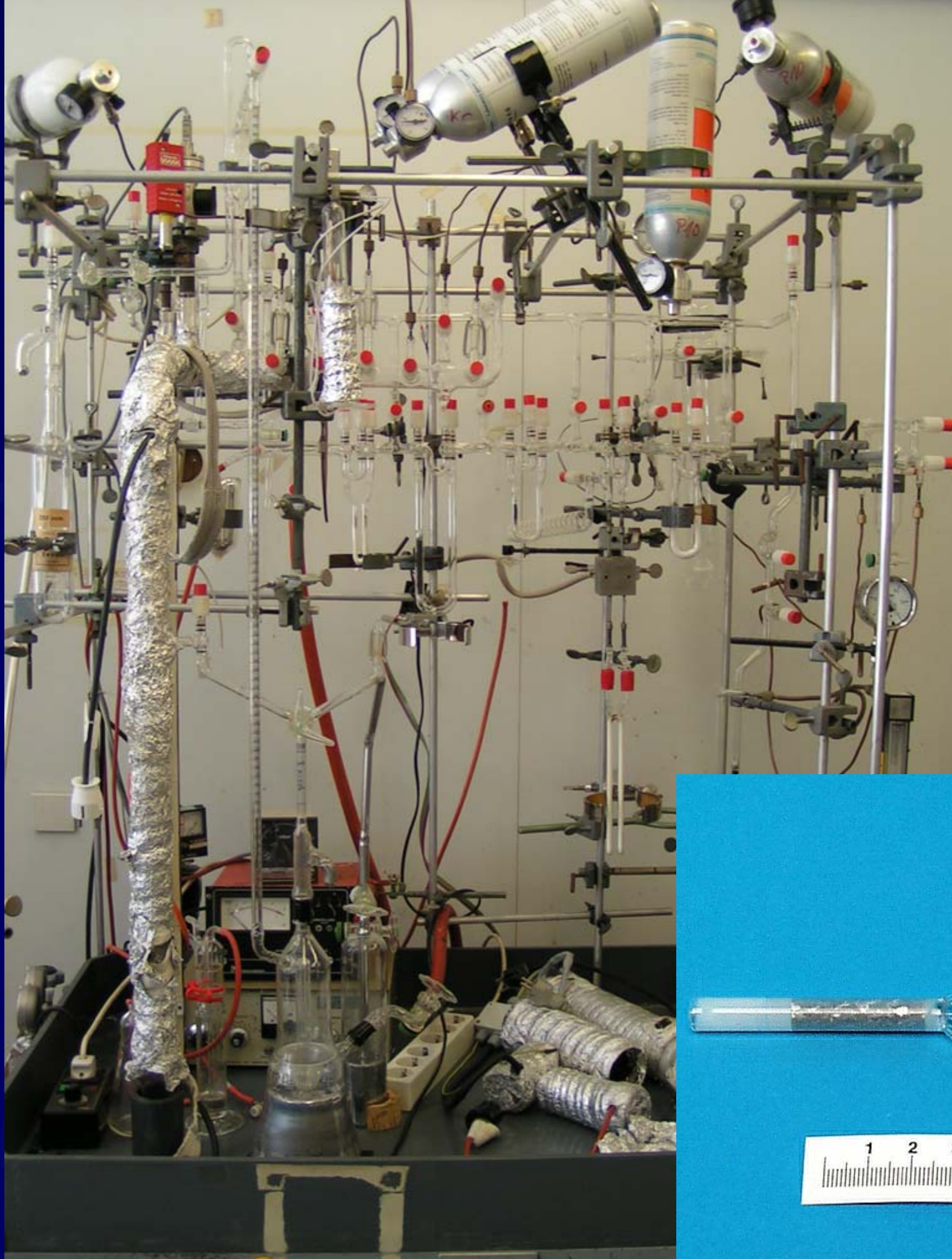
- (Almost) no difference between Ar and N_2 for adsorption on activated carbon
- However T(LAr) = T(LN_2) + 10K
- Rn removal no problem
- Kr removal for Ar even more challenging than for N_2 (especially for large amounts)

Techniques for analysis - Nitrogen -

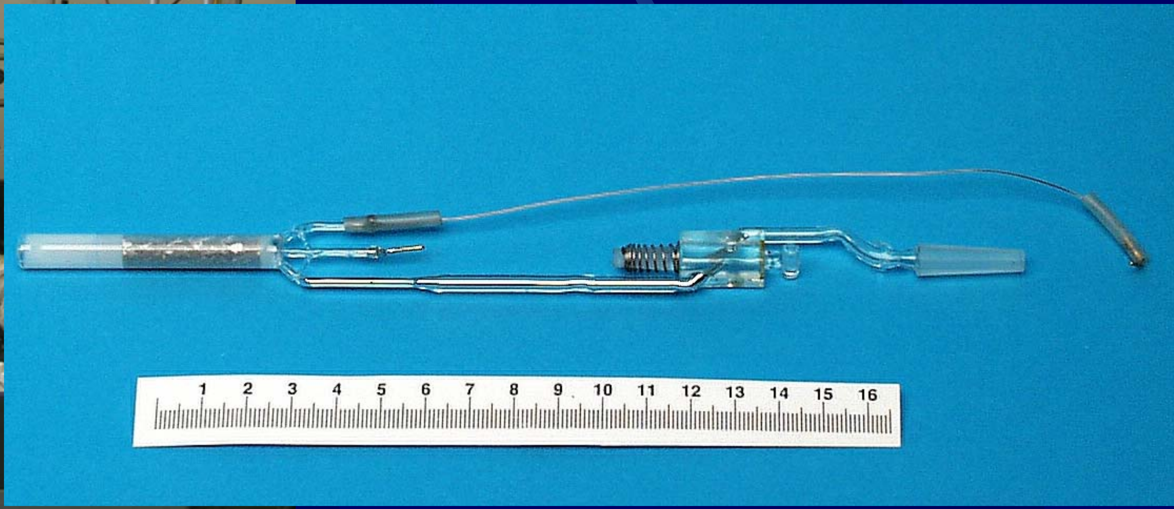
- Rn, Ar, Kr analysis in N_2 performed at MPI-K within BOREXINO
- Rn ↔ low background proportional counters
  - Detection limit: **30 μBq**
- Ar, Kr ↔ noble gas mass spectrometer
  - Detection limits: **1 ppb for Ar**
    0.1 ppt for Kr

Noble gas purification line

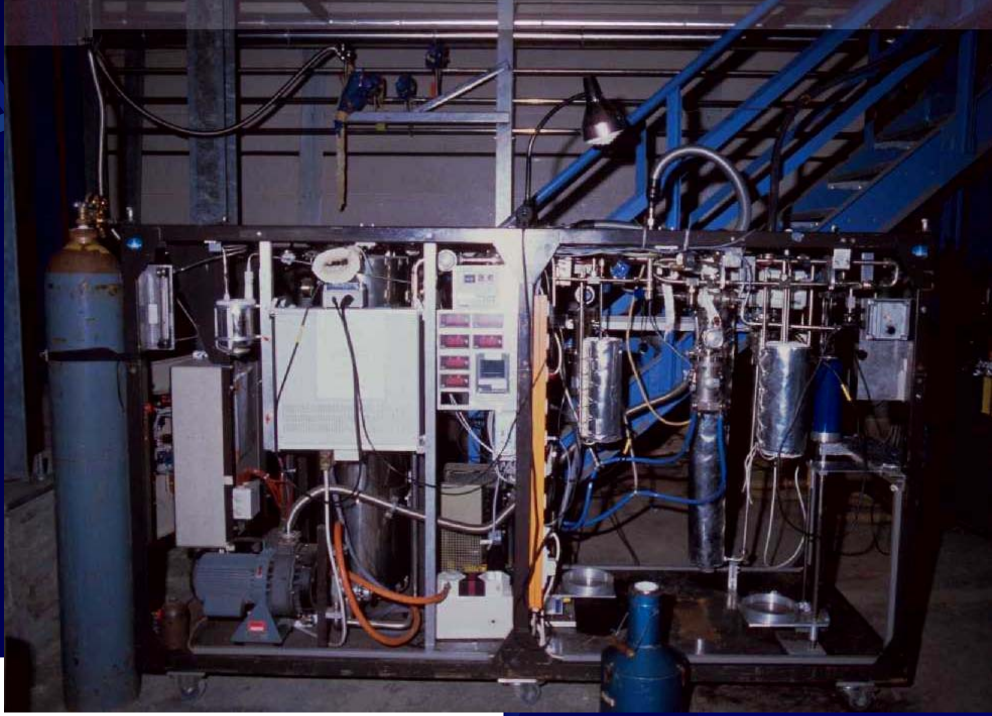


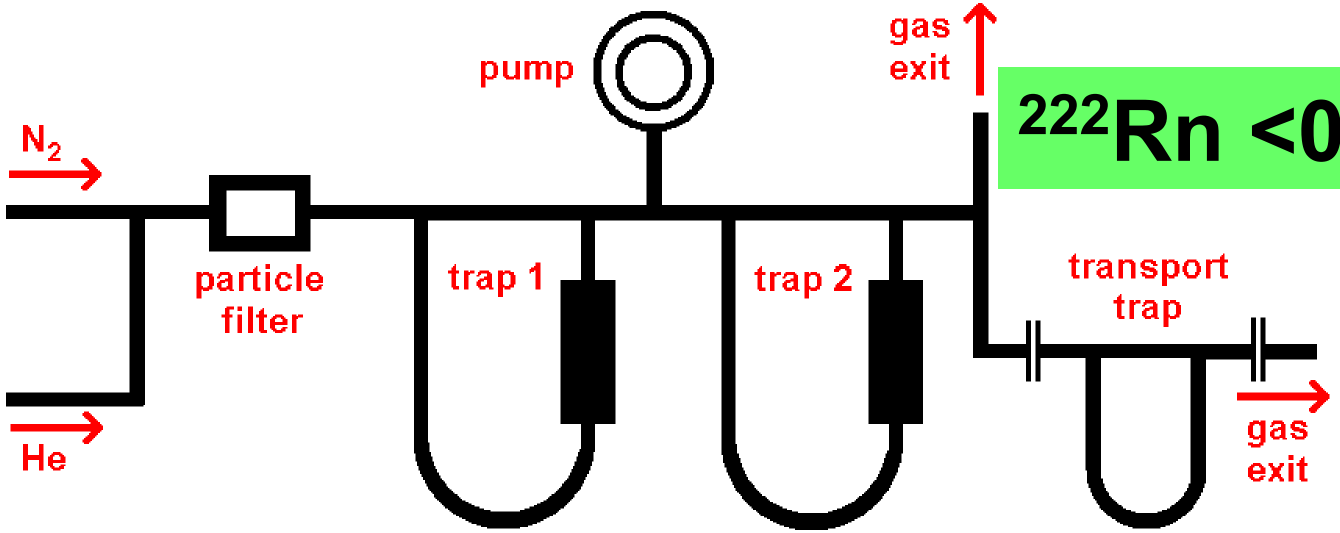


Noble gas purification line



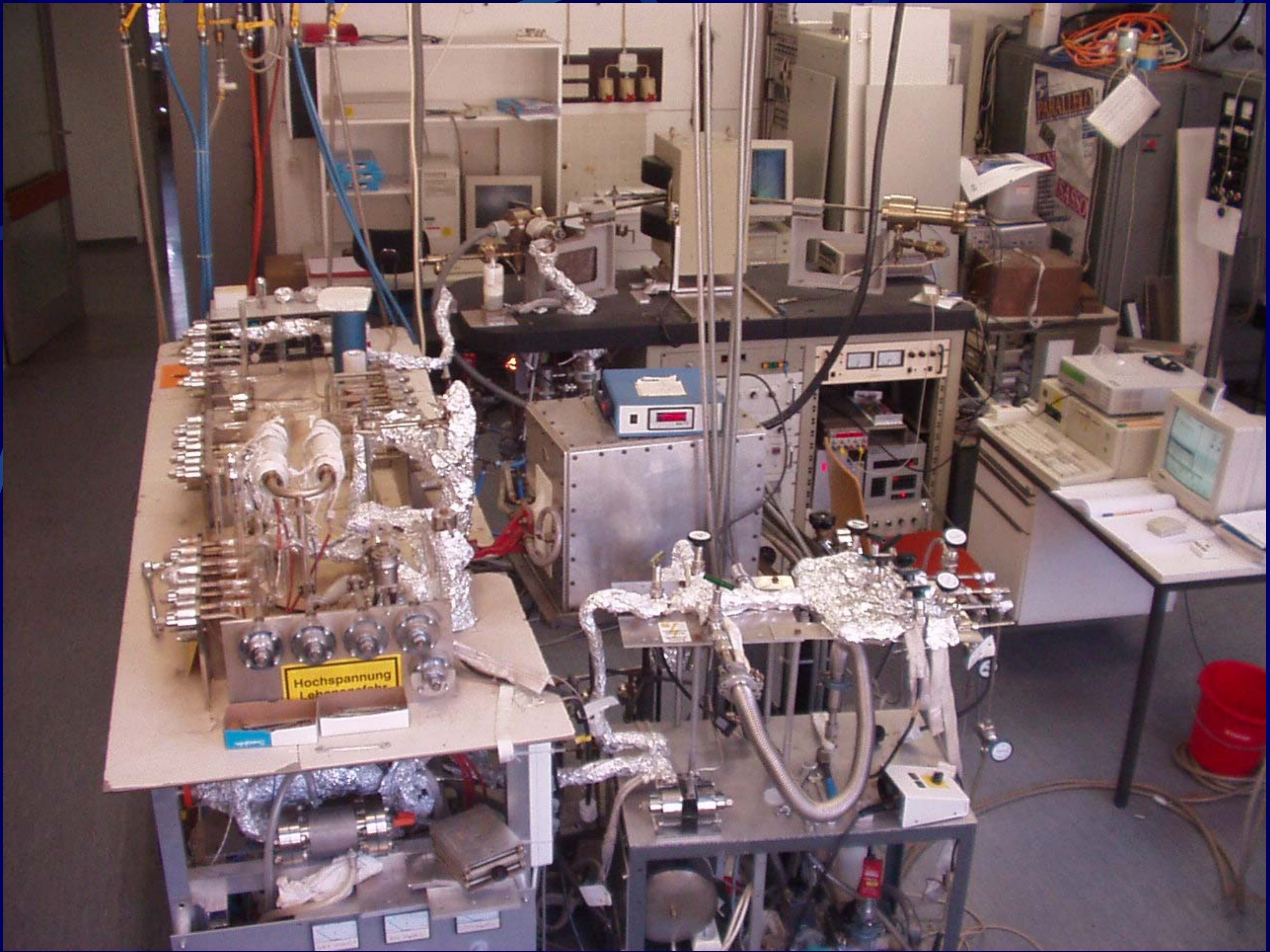
Mobile Radon Extraction Unit (MoREx)





$^{222}Rn < 0.3\ \mu Bq/m^3\ N_2$

Mass spectrometer



Techniques for analysis - Argon -

- Rn analysis in the same way as for N_2
  - Same sensitivity can be achieved
- Kr analysis difficult (contamination of mass spectrometer with Ar)
  - Requires separation of Ar, Kr in advance (gas chromatography)
  - Still some work to do…

Which N_2 is on the market?

Company	Ar [ppm]	Kr [ppt]	^{222}Rn [μBq/m^3]
Air Liquide (4.0)	10	40	~50
Linde (7.0)	0.06	0.3	?
SOL (6.0)	0.005	0.04	?
Westfalen AG (6.0)	0.0005	0.06	?

Which Ar is on the market?

- Ar 6.0 means $\sum$(Contaminants) < 1 ppm
- But noble gases are not included
- N_2, Ar produced in a similar way (rectification)

Reasonable to assume that Kr < 1ppm in Ar can be found on the market

Has to be proven ⇒ Technique for analysis

Summary

- ^{222}Rn requirements similar to BOREXINO
- Kr requirement in Ar ~1ppm
- Adsorption techniques good for highest purities
- Rn in N_2 well under control
  - purification as well as analysis
- Will also work for Rn in Ar

Summary

- Purification of Ar from Kr not trivial
- Recently shown at MPI-K:
  - Purification of N_2 from Kr by adsorption is possible
  - Requires gas phase and special adsorbers
  - Ar purification in the same way, but higher T (10 K)

- Easiest approach: Buy pure enough N_2, Ar
- To do: **Development of technique for measuring 1 ppm Kr in Ar**