Adsorption of radioactives nobles gases in microporous materials

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Radioactive gases in nature

^{3}H (12.3 y)	Cosmogenic Anthropogenic
^{36}Cl (3.10^{5} y)	Comogenic
^{37}Ar (35 d)	Cosmogenic
^{39}Ar (269 y)	Cosmogenic
^{42}Ar (42 y)	Cosmogenic
^{81}Kr (2.310^{5} y)	Cosmogenic
^{85}Kr (10.8 y)	Anthropogenic
^{88}Kr (42.3 d)	Anthropogenic
^{129}I(1.6.10^{7} y)	Anthropogenic
^{133}Xe (5.28 y)	Anthropogenic
^{135}Xe (127.7 d)	Anthropogenic
^{222}Rn (3.8 d)	Natural decay chains (^{235}U, ^{238}U, ^{232}Th)

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Noble gases

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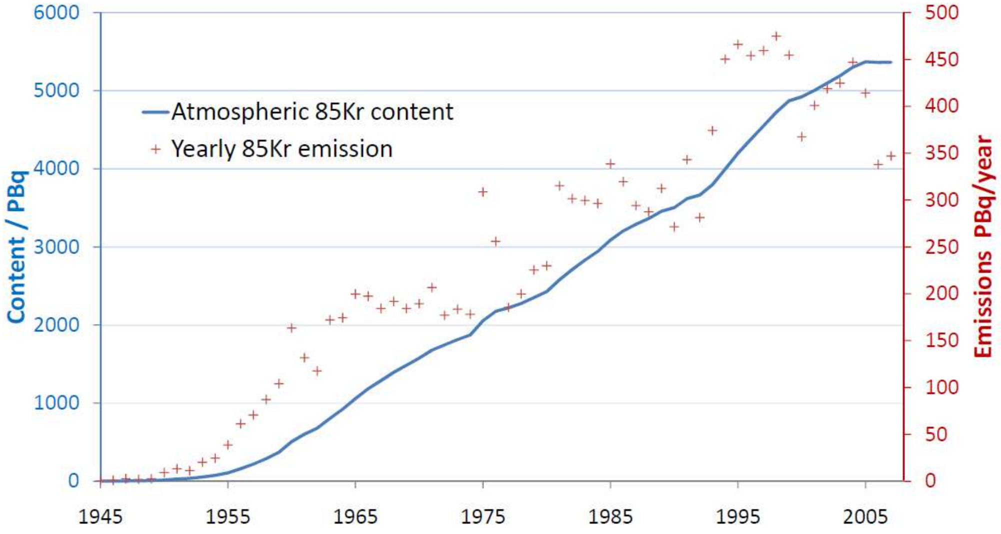
Noble gases

Some noble gases concentration in air

- ☐ ^{39}Ar ⇒ 11 mBq/m^3

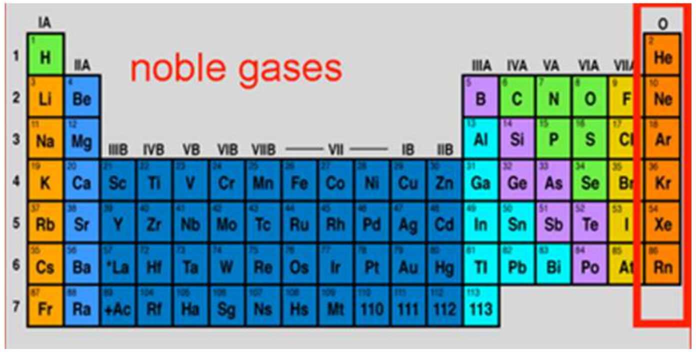
- ☐ ^{85}Kr ⇒ 1 Bq/m^3



Increase 0.025 Bq/m^3/y

- ☐ ^{222}Rn ⇒ 10 -100 Bq/m^3

Capture of noble gases



Noble gases

Full outer shell (8 e^-)

=> no valence electrons

=> very small reactivity

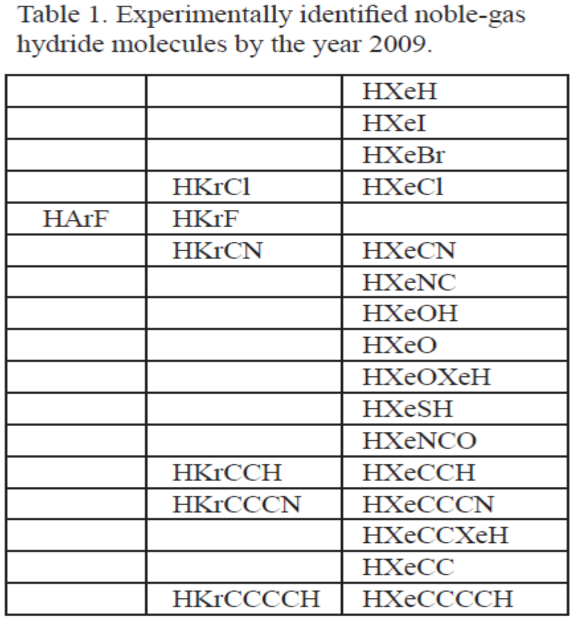


Table 1. Experimentally identified noble-gas hydride molecules by the year 2009.

		HXeH
		HXeI
		HXeBr
	HKrCl	HXeCl
HArF	HKrF	
	HKrCN	HXeCN
		HXeNC
		HXeOH
		HXeO
		HXeOXeH
		HXeSH
		HXeNCO
	HKrCCH	HXeCCH
	HKrCCCN	HXeCCCN
		HXeCCXeH
		HXeCC
	HKrCCCCH	HXeCCCCH

Nevertheless

Possible compounds for heavier noble elements Kr, Xe

Rn must interact with matter better than Xe
However radon is a pure radioactive short period gas
= > poor knowledge of chemical properties

Chemistry of noble gases is possible but very poor

Very difficult capture by chemisorption

Radioactivity from noble gases is an important background for many low-activity low-count experiments

- Krypton (^{85}Kr)

Beta emitter: E_{max} = 687 keV, γ of 514 keV @ 0.43 %

- Argon (^{39}Ar)

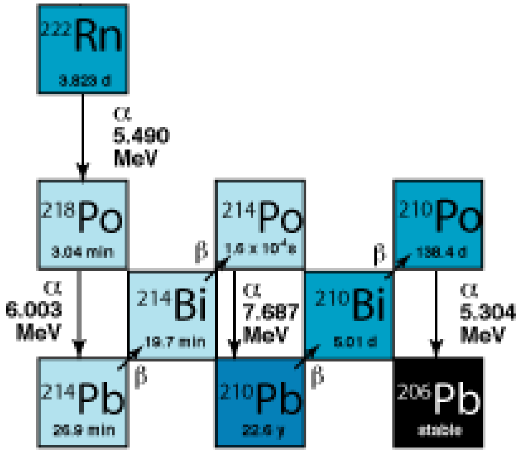
Beta emitter: E_{max} = 565 keV, no gamma!

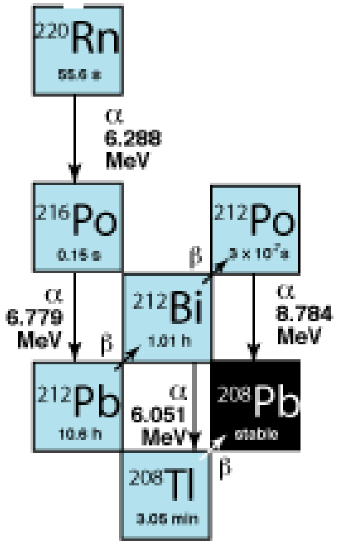
- Radon (^{220}Rn, ^{222}Rn)

Alpha emitter up to 8.8 MeV

Beta emitter up to 5 MeV

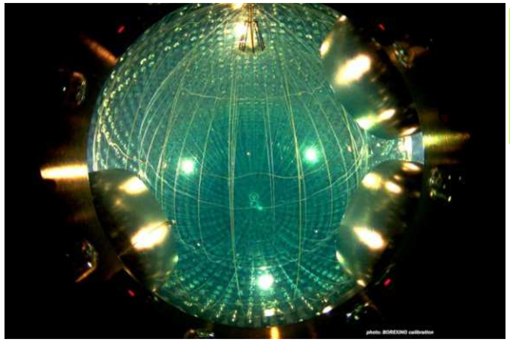
Gamma up to 2.6 MeV





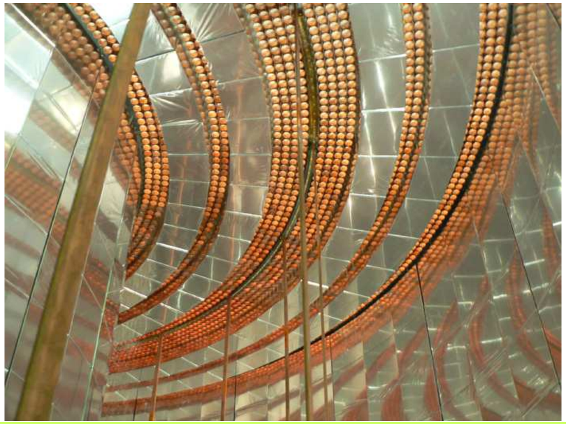
Radioactivity from noble gases is an important background for many low-activity low-count experiments

Borexino Solar Neutrino experiment



^{85}Kr → < 0.2 μBq/m^3
^{39}Ar → < 0.5 μBq/m^3

SuperNEMO $\beta\beta$ experiment

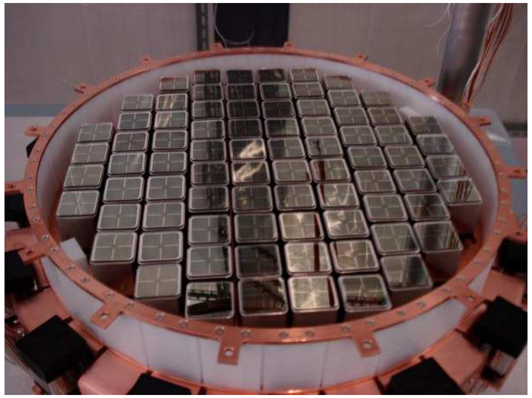


^{222}Rn → < 150 μBq/m^3 (< 100 atoms / m^3)

Gerda $\beta\beta$ experiment

^{42}Ar → < 40 μBq/L

LUX dark matter experiment



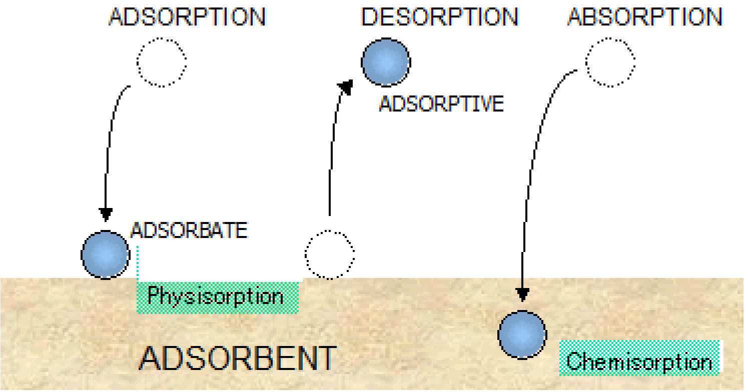
^{85}Kr → < 2 ppt

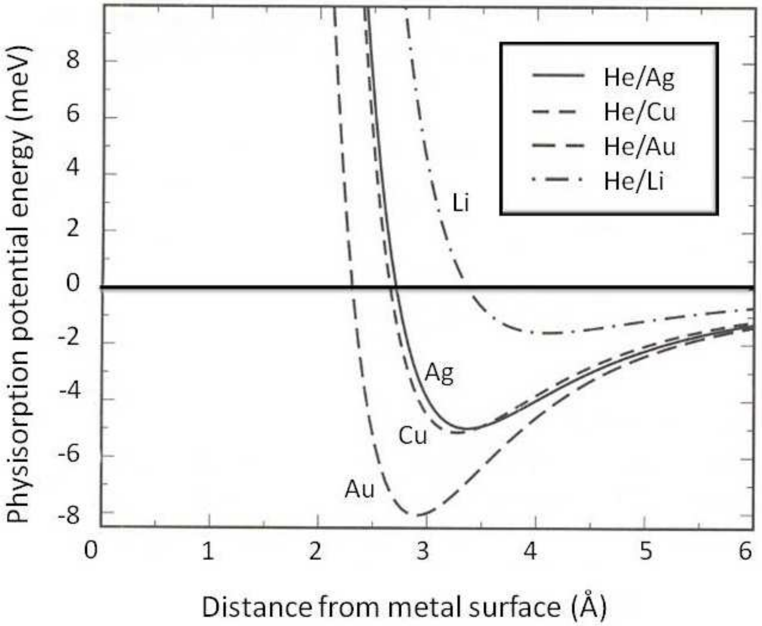
Nobel gases adsorption

Nobel gas => capture mainly by physisorption (adsorption)

→ Weak Van der Waals

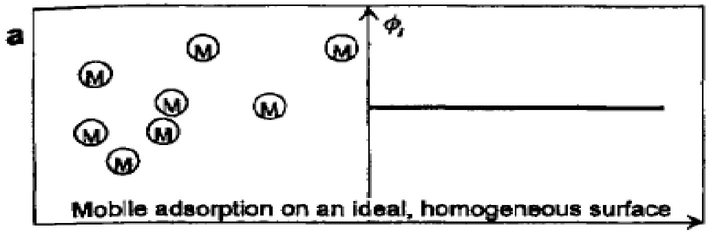
Capture on surface



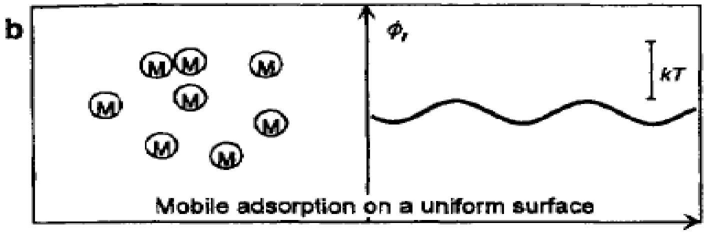


Equilibrium between Adsorption and Desorption

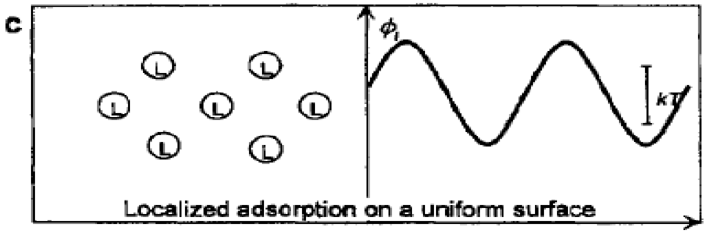
Transport of adsorbed molecules



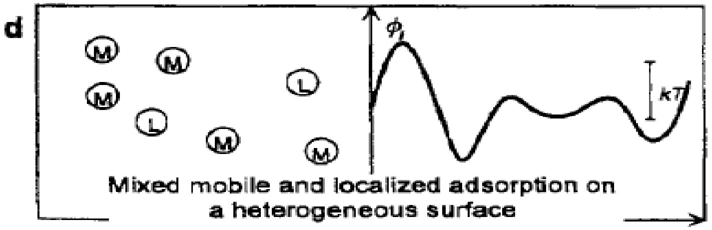
Mobile adsorption on an ideal, homogeneous surface



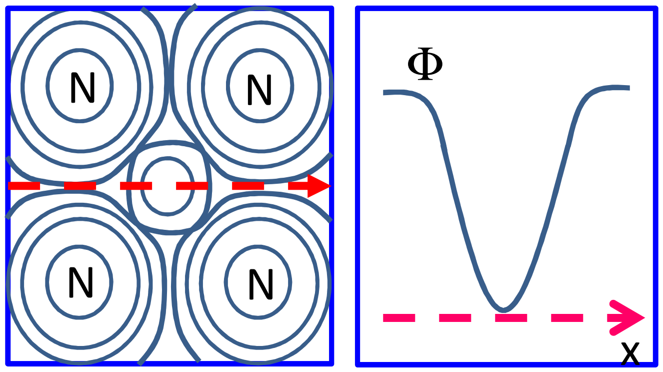
Mobile adsorption on a uniform surface



Localized adsorption on a uniform surface



Mixed mobile and localized adsorption on a heterogeneous surface



Potential well

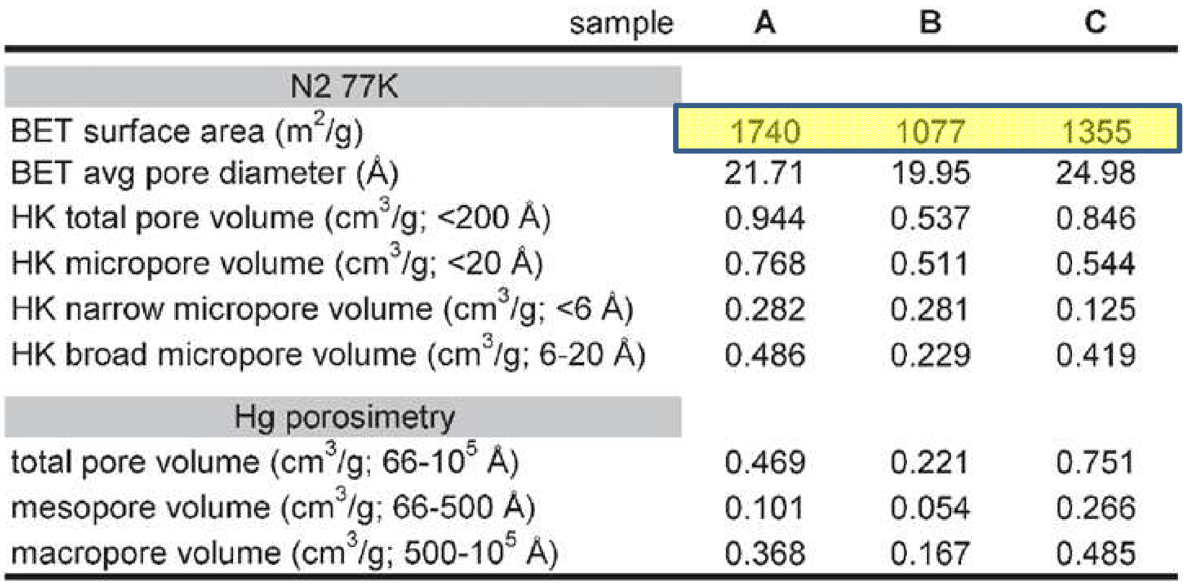
If Φ is much smaller than thermal energy , kT, the molecules are regarded as “mobile”.

If Φ is much larger than kT, the molecules are “localized”.

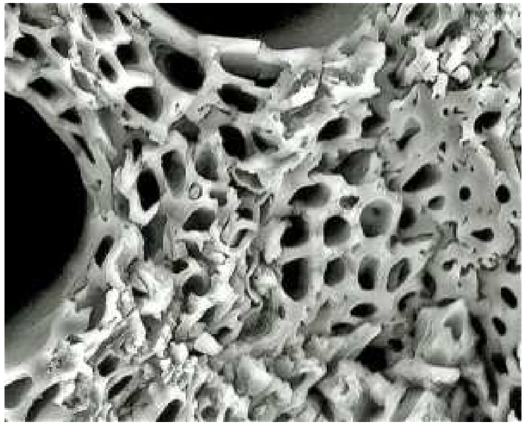
To increase the capture capacity we need :

- **increase the surface area => high porosity**
- **reduced the temperature**

Typical porosity of active charcoals :



sample	A	B	C
N2 77K			
BET surface area (m^2/g)	1740	1077	1355
BET avg pore diameter (Å)	21.71	19.95	24.98
HK total pore volume (cm^3/g; <200 Å)	0.944	0.537	0.846
HK micropore volume (cm^3/g; <20 Å)	0.768	0.511	0.544
HK narrow micropore volume (cm^3/g; <6 Å)	0.282	0.281	0.125
HK broad micropore volume (cm^3/g; 6-20 Å)	0.486	0.229	0.419
Hg porosimetry			
total pore volume (cm^3/g; 66-10^5 Å)	0.469	0.221	0.751
mesopore volume (cm^3/g; 66-500 Å)	0.101	0.054	0.266
macropore volume (cm^3/g; 500-10^5 Å)	0.368	0.167	0.485



Enormous surface area of active charcoal

The effective surface area is distributed between different porous size

Pore size and atomic radious

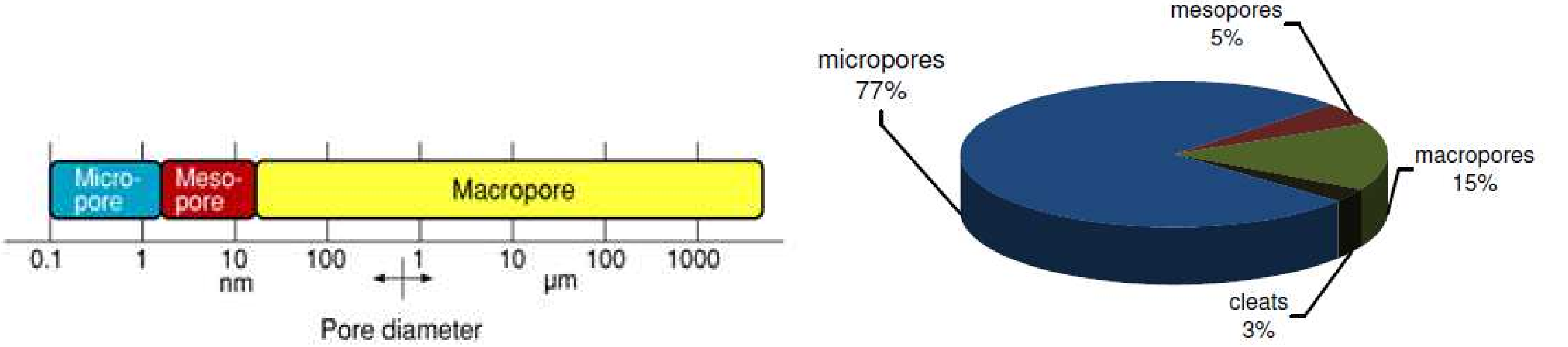


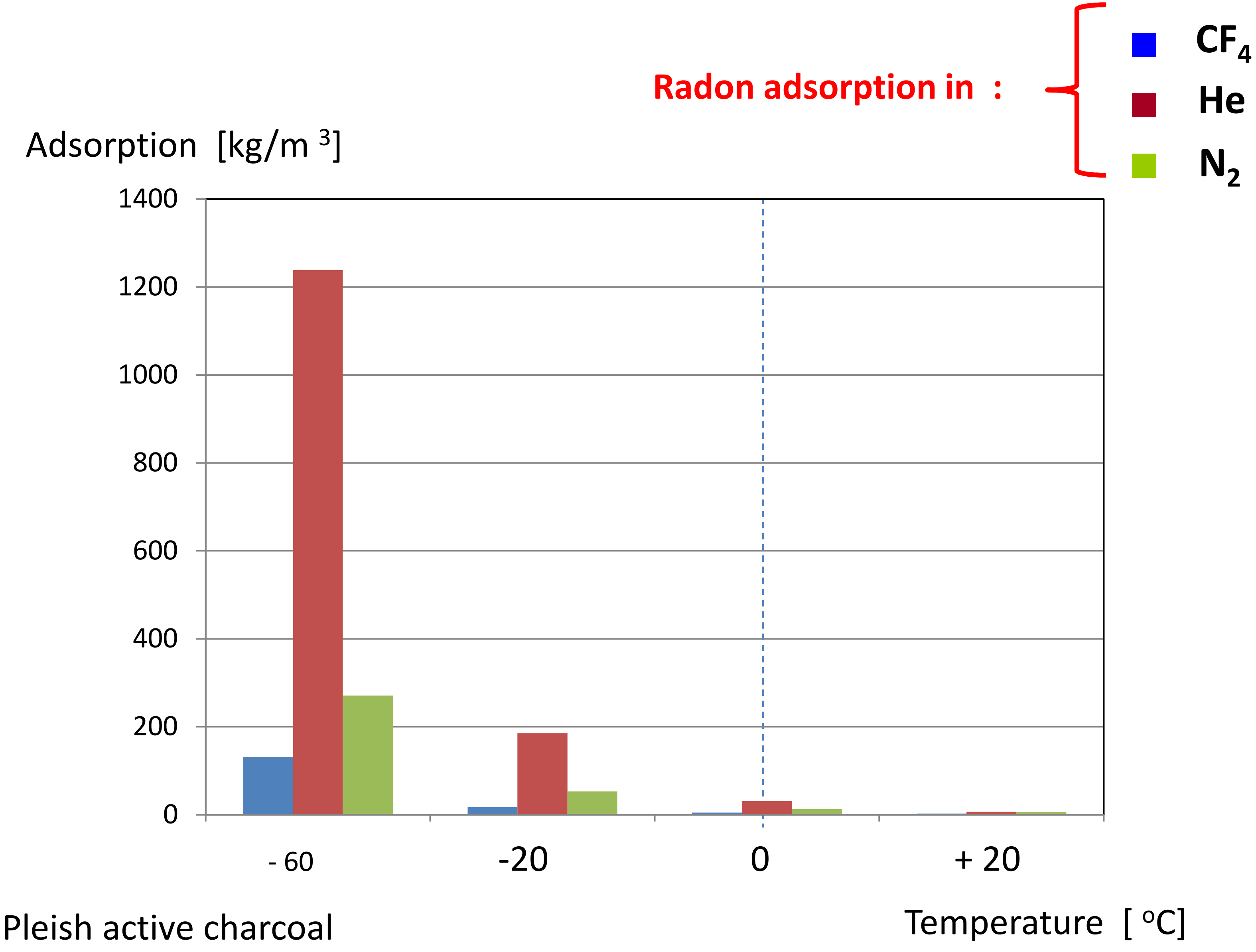
Figure 3.1: Example Pore Size Distribution in Coal (Mardon 2008)

Gas	van der Waals	Covalent (single bond)	Covalent (triple bond)
	nanometer		
He	0.14	0.032	-
N	0.155	0.075	0.054
Ar	0.188	0.097	0.096
Kr	0.202	0.110	0.108
Xe	0.216	0.130	0.122
Rn	0.220	0.145	0.133

Atomic radious

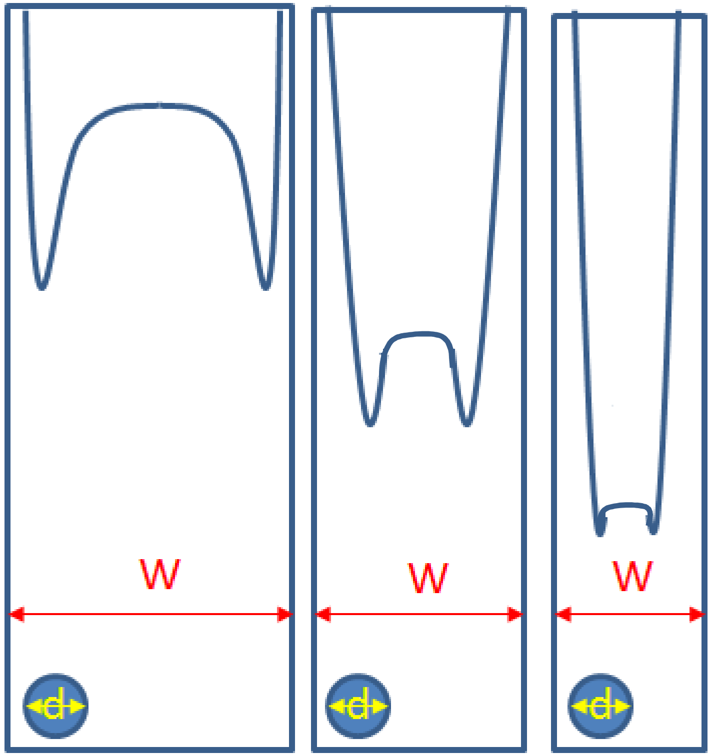
Competition between carrier gas and radon

Adsorption competition



Enhancement of the energy of adsorption in slit shaped pores of various widths

Van der Waals potential well in a narrow porous

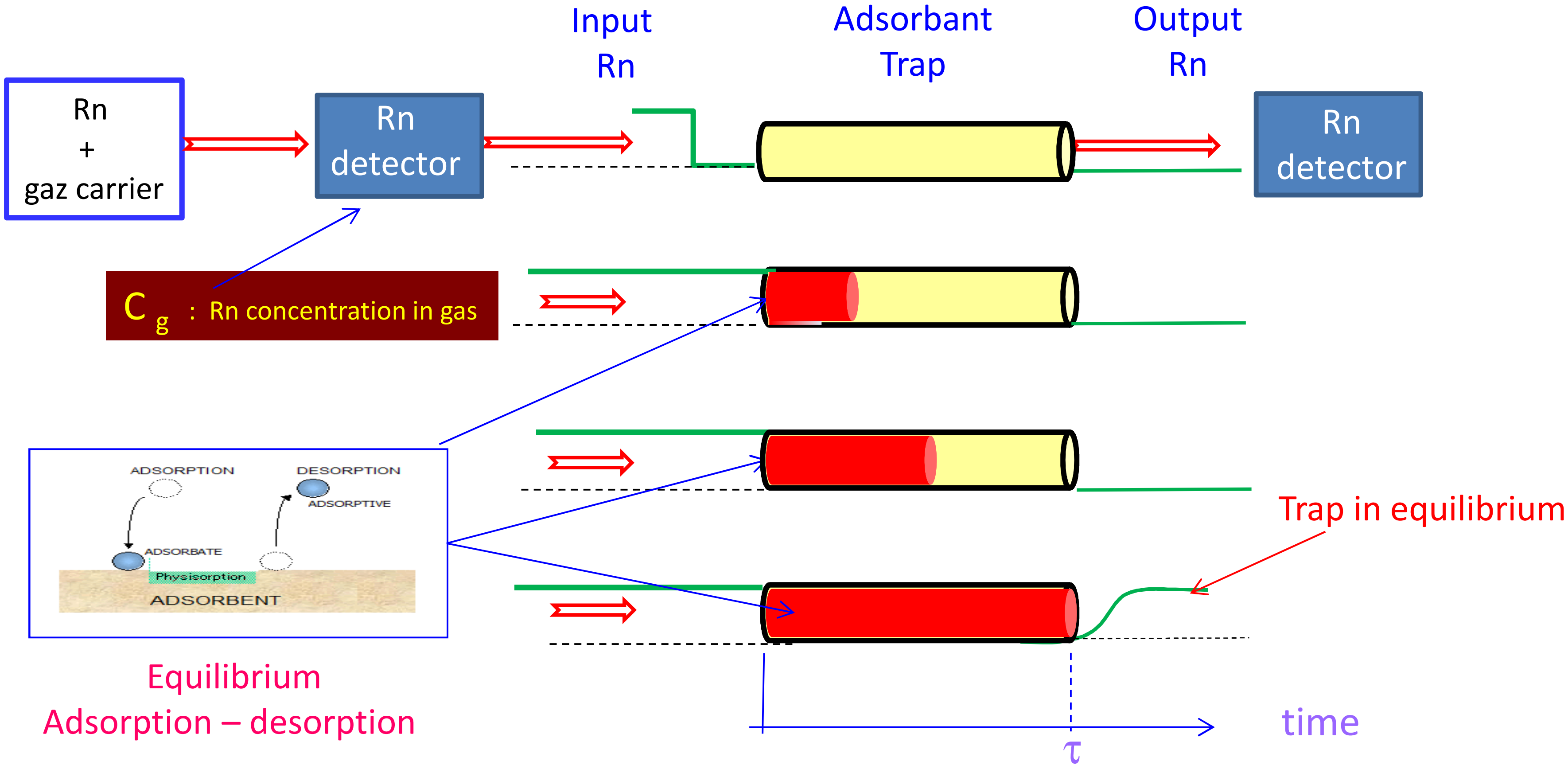


The size and the shape of the pores has to be optimum

Radon capture measurements at CPPM

Characterization of radon adsorption on microporous materials

Radon capture measurement by dynamic technique



Rn + gaz carrier

Rn detector

Input Rn

Adsorbant Trap

Output Rn

Rn detector

C $_g$: Rn concentration in gas

Equilibrium
Adsorption – desorption

Trap in equilibrium

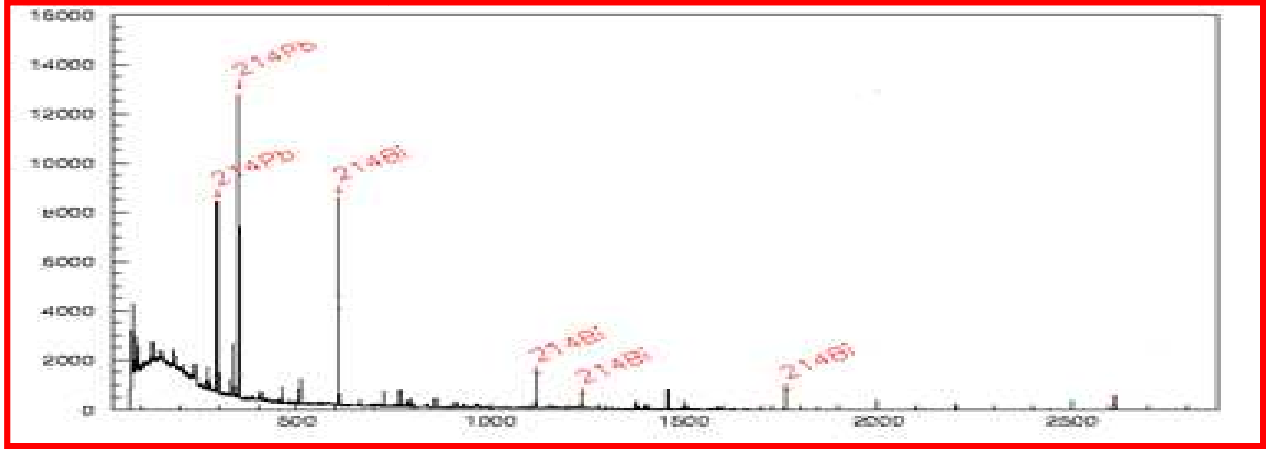
τ

time

Radon capture measurement by dynamic technique

C_m : Rn concentration in the trap

Radon in filter material by γ-Ge spectrometry

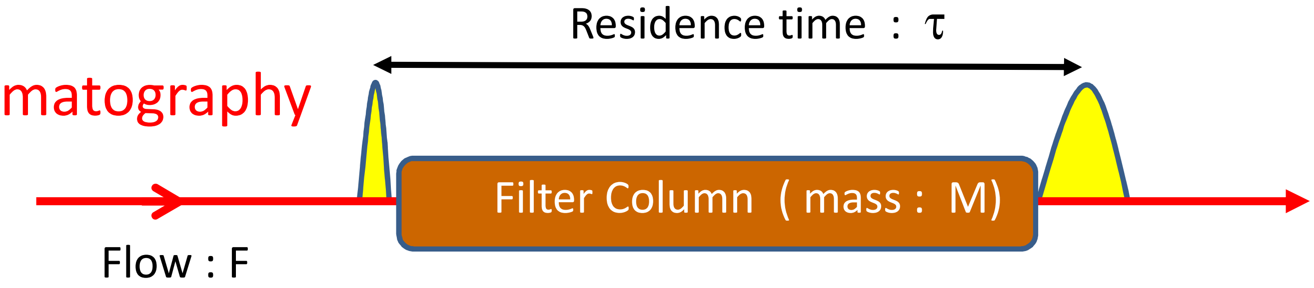


Radon concentration

$$K\ [m^3/kg] = \frac{Rn\ activity\ in\ the\ \mathrm{trap}[Bq/\mathrm{kg}]}{Rn\ activity\ in\ the\ gas[Bq/m^3]}$$

Residence time v. s. adsorption capacity

From gas chromatography



Residence time : τ

Filter Column (mass : M)

Flow : F

Mass

$$\boxed{\tau = \frac{K_{chr} \cdot M}{F}}$$

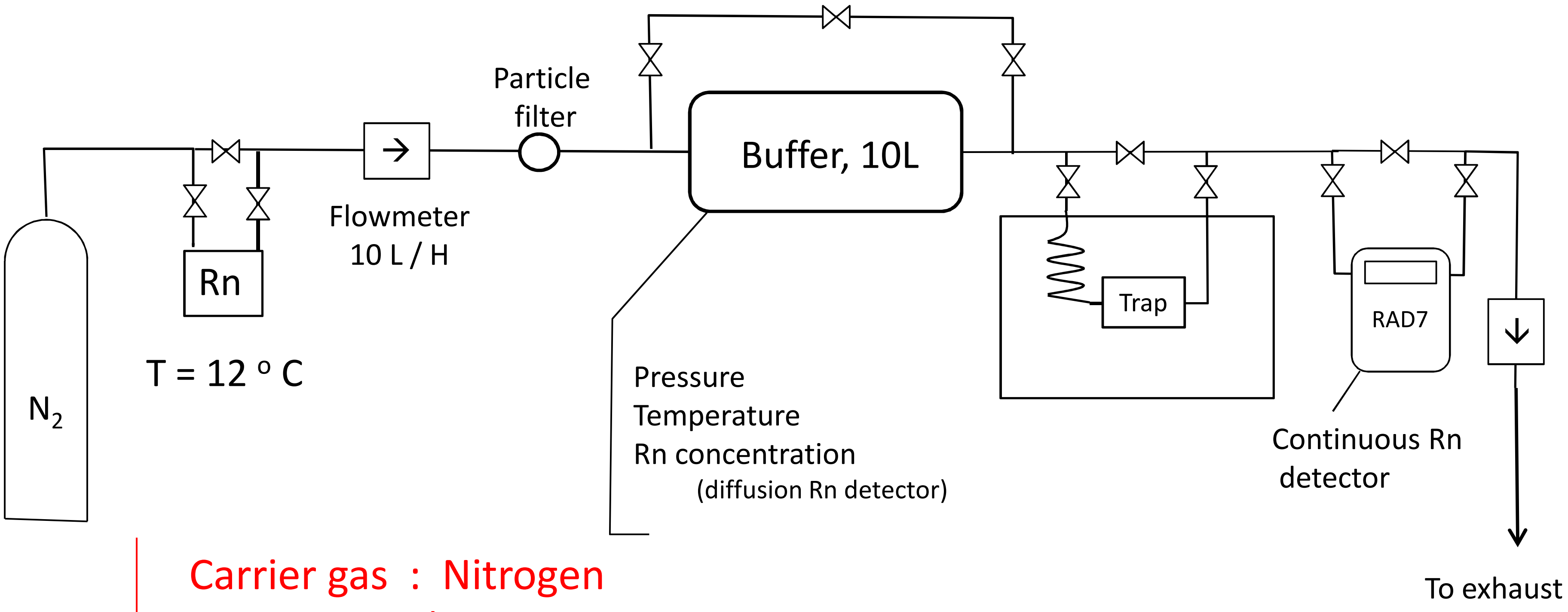
Flow

If K is big enough => τ >> $T_{1/2}$(Rn)

the Rn concentration after the radon trap is be negligible

Experimental setup

Dynamic Rn adsorption



Carrier gas : Nitrogen
Flow : 10 L / H
Rn concentration : ~ 900 Bq / m^3
Trap temperature : + 20 °C to – 80 °C
Pressure : 1 bar

Measured materials

T = 20 °C, -30 °C, -50 °C, - 80 °C
P = 1 bar
Gas = Nitrogen, He

- Classical activated carbon : very wide pore size distribution
- Synthetic carbon : Carboact “popular” adsorbent in Low Radioactive Experiments
- Carbon molecular sieve : well defined pore size
- Metal Organic Framework : very large surface area
- Molecular Cages : well defined structue
- Zeolites : well defined structure; not low background
- Aerogel : large surface areas

Results Active charcoal in N2

	température C					
	20		-30		-45	
Echantillons	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur
K48 SPECIAL	12,5	1,8	92,4	3,5	347,9	10,3
K48	10,0	1,6	61,4	2,8	271,5	12,0
ZORFLEX FM100	13,4	3,3	57,9	3,3	266,3	7,7
NUCLEARCARB 208C 5KI3	6,9	1,3	43,3	2,5	209,5	7,0
K610	6,2	1,3	22,1	2,6	170,2	6,0
NUCLEARCARB 208C 5TEDA	3,9	1,2	29,9	2,1	97,5	4,3
ENVIRONCARB 207C	2,2	1,0	12,1	1,7	49,1	3,3

Results

Carbon Molecular Sieve, CARBOACT
MOF in N2

	température C					
	20		-30		-45	
Echantillons	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur
CARBOSEIVE SIII	10,0	6,1	168,4	9,5	728,5	32,9
CARBOSIEVE G			81	6,5		
CARBOXEN 1000	10,8	8,4	80,8	6,7	645,3	27,9
CARBOXEN 1012			150	7,6		
CARBOXEN 1020			82	6,1		
CARBOXEN 1018			136	8,2		
CARBOXEN 569	2,2	6,3	9,7	3,9	99,8	5,7
CARBOACT	20,5	2,9	131,9	4,1	425,5	11,4
MOF Basolite C300	8,7	4,8	215,2	10,3	409,2	10,6

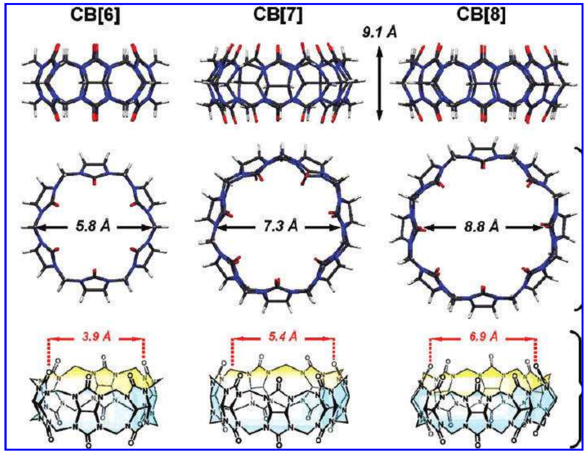
Big surface area. Very fine powder

Very low background

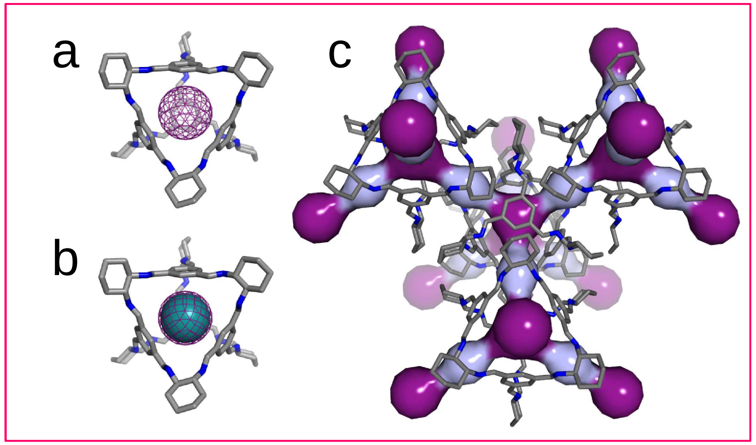
Well defined porosity

Results molecular cages in N2

	température C					
	20		-30		-45	
Echantillons	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur
CB[6]	1,4	7,4	1,1	3,8	19,9	9,9
CB[7]	5,0	7,1			10,3	10,1
CB[8]	8,1	9,2			5,2	6,2
PYR C7	2,5	8,7			4,6	4,7
REC10	4,6	9,9			2,6	5,5
C3 cage	6	7,1	25	3,2	89,9	4,2



Curcubiturils

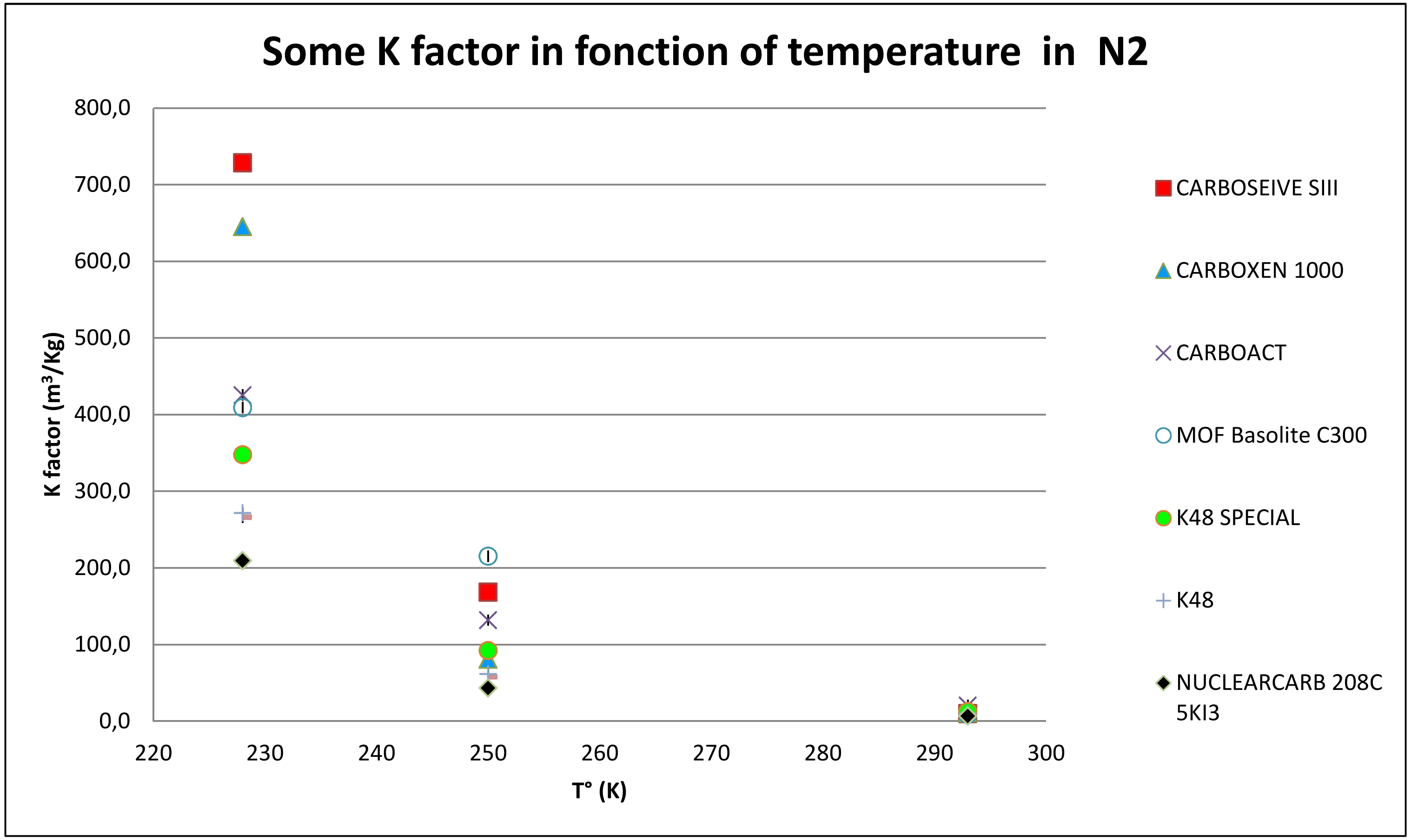


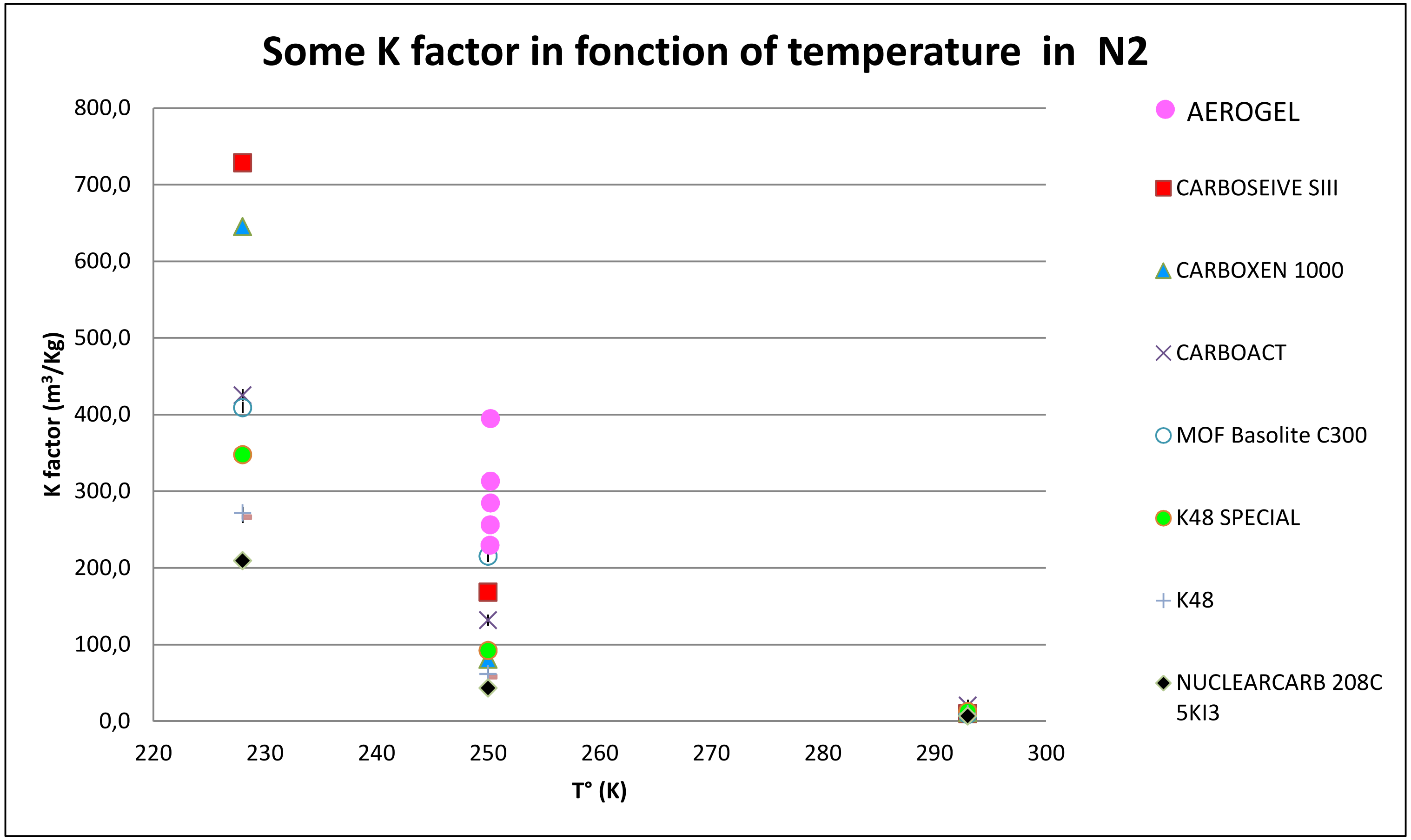
Porous organic cages CC3

Results Carbon aerogel in N2

	température C			
	20		-30	
Echantillons	K factor(m3/Kg)	erreur	K factor(m3/Kg)	erreur
AEROGEL D			298	11
AEROGEL J			250	10
AEROGEL K			220	10
AEROGEL K11			317	13
AEROGEL J18			380	13

Very promising adsorbent


Some K factor in fonction of temperature in N2
K factor (m³/Kg)
800,0
700,0
600,0
500,0
400,0
300,0
200,0
100,0
0,0
220
230
240
250
260
270
280
290
300
T° (K)
CARBOSEIVE SIII
CARBOXEN 1000
CARBOACT
MOF Basolite C300
K48 SPECIAL
K48
NUCLEARCARB 208C 5KI3


Some K factor in fonction of temperature in N2

Results in He

	-30		-50		-80	
Echantillons	K factor(m3/Kg)		K factor(m3/Kg)		K factor(m3/Kg)	
G2X4 (XMASS Charcoals)			2102+-60		6800+-240	
CARBOXEN 1012			5672+-220		8000+-350	
K48 special			2553+-85			
K48			2200+-60			
CARBOACT			7865+-280			
CARBOSIEVE III			9900+-370			
Aerogel D	1840+-64		4450+-160			
Aerogel J			5400 +- 230			
Aerogel K			6900 +- 250			
Aerogel K11			8300 +- 320			
Aerogel J18						

Very low competition between Rn and He

Very long measurements : ~ 10 days @ - 50 °C, 10 L /h and 0.3 gr

Randon capture v.s. porosity

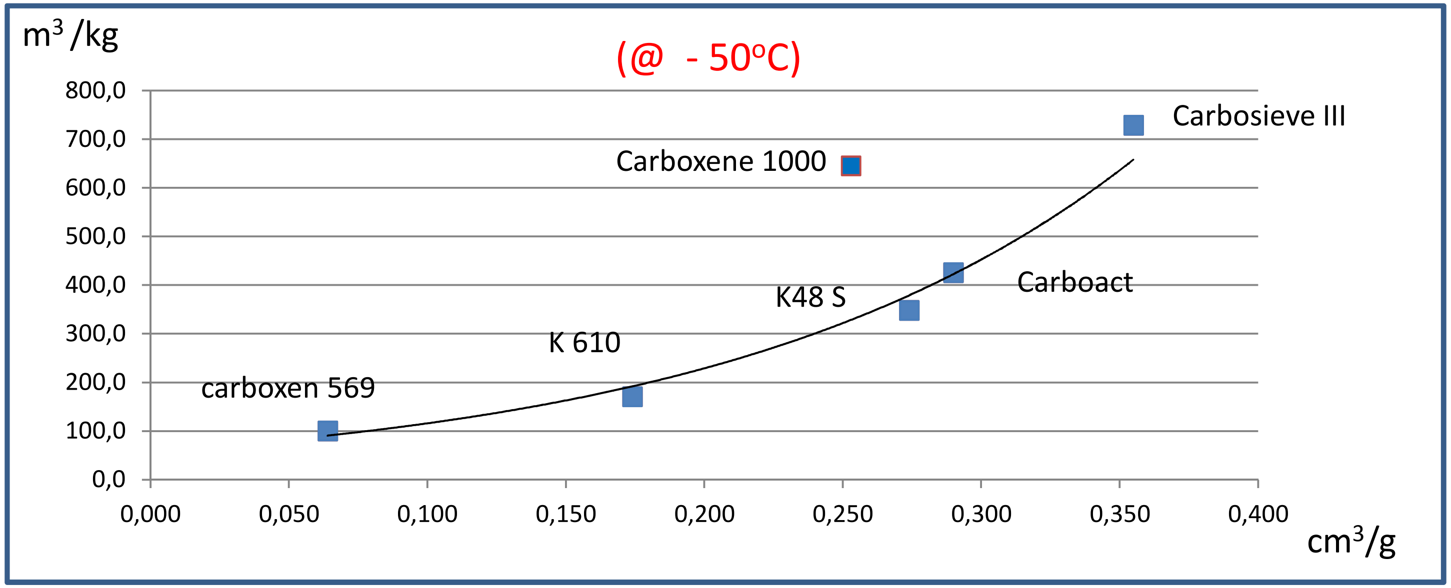
			Volume microporeux total			Volume ultramicro	% ultra	Volume supermicro	Aext
Echantillons	A_{BET}	Volume total	t-plot	α_s-plot	DR	α_s-plot		α_s-plot	$m^2.g^{-1}$
	$m^2.g^{-1}$	$cm^3.g^{-1}$	$cm^3.g^{-1}$	$cm^3.g^{-1}$	$cm^3.g^{-1}$	$cm^3.g^{-1}$		$cm^3.g^{-1}$	
K610	940	0,381	0,370	0,410	0,348	0,174	42	0,236	40
Carboxen 569	290	0,484	0,080	0,064	0,117	0,064	100	0,000	164
Pleisch(CH)	1340	0,613	0,553	0,563	0,506	0,291	52	0,272	31
K48 special	1268	0,512	0,505	0,507	0,520	0,274	54	0,233	5
Carboact	1182	0,534	0,470	0,462	0,476	0,290	63	0,172	26
Carboxen 1000	931	0,842	0,357	0,359	0,366	0,253	70	0,106	20
Carbosieve SIII	1362	0,565	0,510	0,510	0,535	0,355	70	0,155	8

Ultramicropore :

diamètre<1,062 nm

Adsorption v. s. microscopic properties

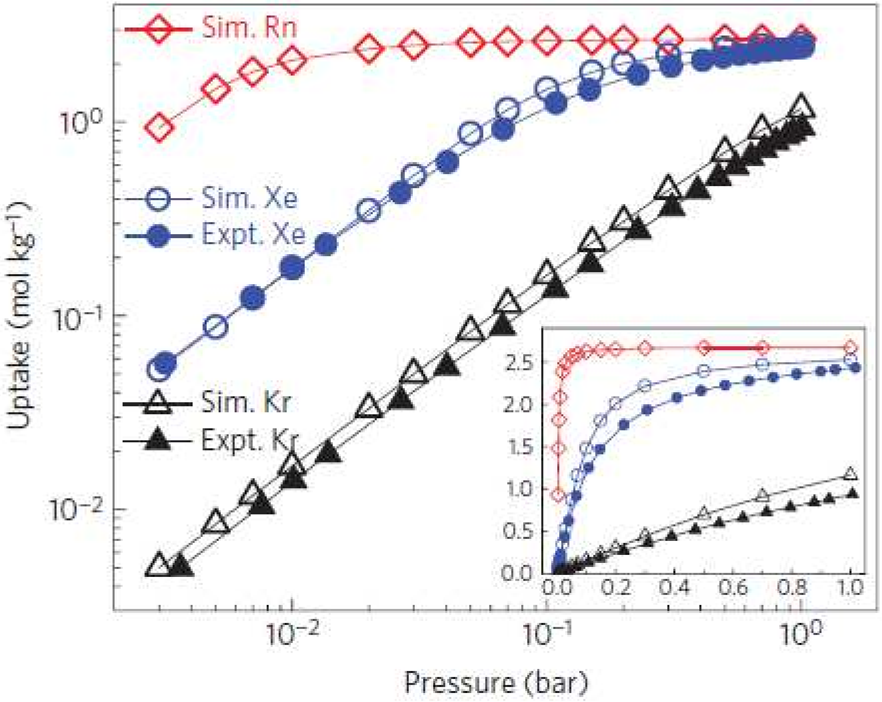
Adsorption (m³ /kg) v.s volume of ultramicropores (< 1.62 nm)

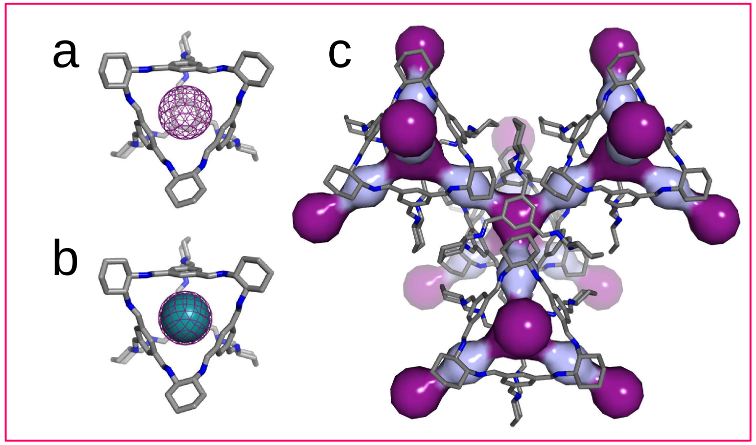


Very good correlation

$\Rightarrow$ **Modelization of radon adsorption**

Modelization is possible in “symmetric” carbon cages

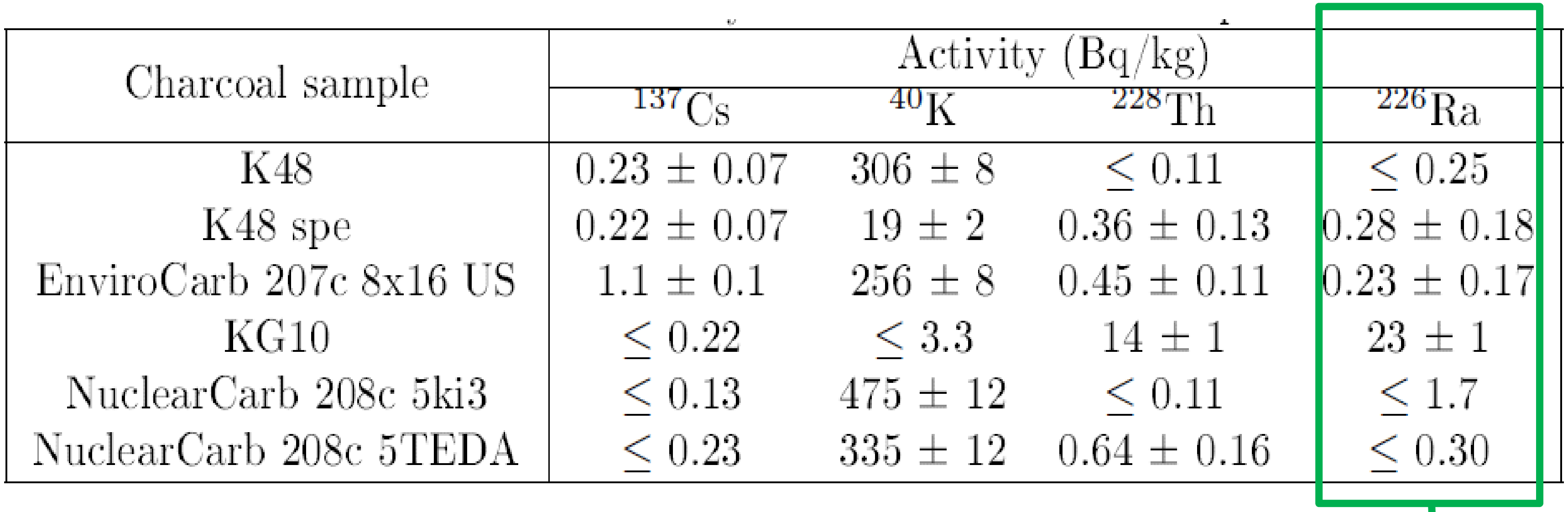




Predicted adsorption isotherme
for Kr, Xe and Rn

Self emanation

Radioactivity of some active charcoals



Charcoal sample	Activity (Bq/kg)			
	^{137}Cs	^{40}K	^{228}Th	^{226}Ra
K48	0.23 ± 0.07	306 ± 8	$\lesssim 0.11$	$\lesssim 0.25$
K48 spe	0.22 ± 0.07	19 ± 2	0.36 ± 0.13	0.28 ± 0.18
EnviroCarb 207c 8x16 US	1.1 ± 0.1	256 ± 8	0.45 ± 0.11	0.23 ± 0.17
KG10	$\lesssim 0.22$	$\lesssim 3.3$	14 ± 1	23 ± 1
NuclearCarb 208c 5ki3	$\lesssim 0.13$	475 ± 12	$\lesssim 0.11$	$\lesssim 1.7$
NuclearCarb 208c 5TEDA	$\lesssim 0.23$	335 ± 12	0.64 ± 0.16	$\lesssim 0.30$

Radon emanation from the trap it self

- *Very pure adsorbent (synthetic materials)*
- *Mass of adsorbent as low as possible*

→ *Self adsorption can help*

Conclusion

- Radioactivity from noble gases is an important background source in many low energy and low count rate experiments.

- Adsorption in microporous materials is possible but depends on porosity characteristics and carrier gas competition.