CArbon-14 Source Term
CAST

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Outline

Separation and analysis of gaseous/dissolved C-14 compounds in structural parts of irradiated LWR fuel elements

Training Course
C-14 behaviour under repository conditions

July 05–06, 2016, Karlsruhe, Germany

- Introduction
- Materials and irradiation characteristics
- Preparation of subsamples
- Dissolution experiments involving Zircaloy-4 and stainless steel
- Extraction of ^{14}C from gaseous and aqueous samples
- Methods (LSC, gas-MS, γ-spectroscopy)
- MCNP calculations
- Results

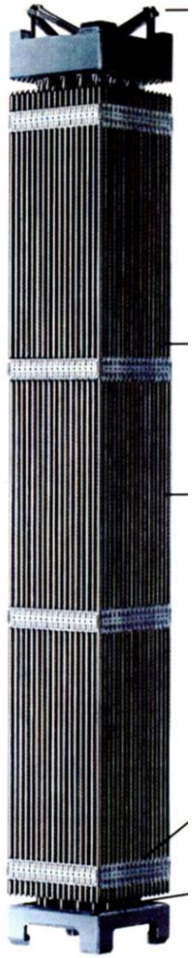
Introduction

- ^{14}C is a key radionuclide in safety assessments of geological disposal systems for nuclear waste
- Chemical form of ^{14}C upon release unknown and $t_{1/2}$ = 5730 a
  → ^{14}CO, $^{14}CO_2$, gaseous/dissolved hydrocarbons
- Speciation crucial to assess mobility/retention of ^{14}C upon release
  → gaseous/dissolved hydrocarbons hardly retained in technical/geo-technical barriers
- Until now: transfer of total ^{14}C inventory to biosphere considered in safety assessments

Introduction

- Physical formation of ^{14}C in fuel assemblies by
  - neutron capture reactions
  - ternary fission in the fuel

  during reactor operation



$^{14}_{7}N(n,p)^{14}_{6}C$	$^{14}_{7}N + {}^{1}_{0}n \rightarrow [^{15}_{7}N]^{*} \rightarrow {}^{14}_{6}C + {}^{1}_{1}p$
$^{17}_{8}O(n,\alpha)^{14}_{6}C$	$^{17}_{8}O + {}^{1}_{0}n \rightarrow [^{18}_{8}O]^{*} \rightarrow {}^{14}_{6}C + {}^{4}_{2}He$
$^{13}_{6}C(n,\gamma)^{14}_{6}C$	$^{13}_{6}C + {}^{1}_{0}n \rightarrow [^{14}_{6}C]^{*} \rightarrow {}^{14}_{6}C + \gamma$

ternary fission in LWR fuel	1.7×10^{-6} per thermal ^{235}U fission 1.8×10^{-6} per thermal ^{239}Pu fission

Introduction

- N and C are present as impurities in fuel, Zircaloy cladding and structural parts of LWR fuel assemblies
- ^{17}O is a stable low-abundance, naturally occurring istope
- Exemplary N impurities and calculated ^{14}C inventories of spent PWR fuel assemblies with an average burn-up of about 50 GWd/t_{HM}:

material	N impurity [ppm]	calculated ^{14}C inventory [Bq/g]
PWR SNF	~10	~27200
Zircaloy-4	~40	~30000
stainless steel	~500	~80000

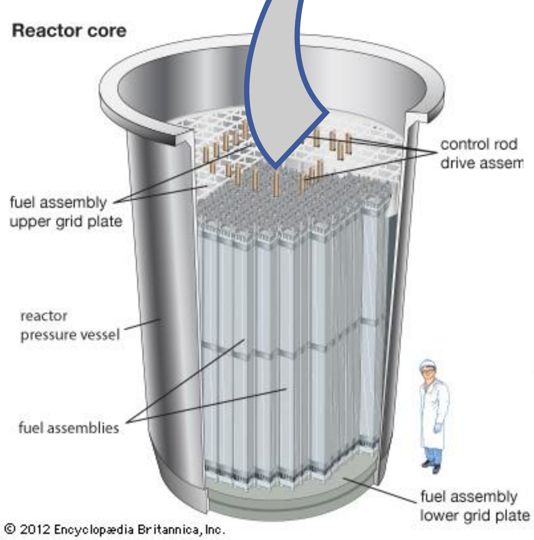
Introduction

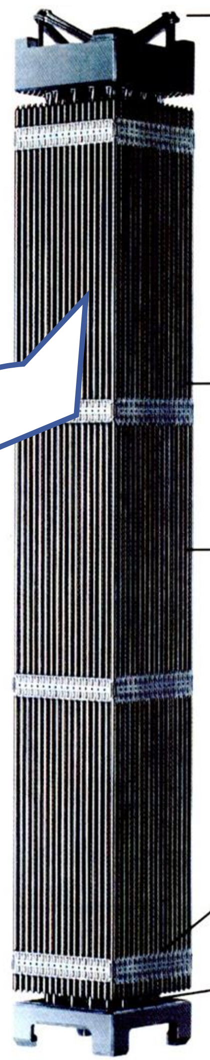
- N, C in Zircaloy / stainless steel **before** irradiation is potentially present as
  - interstitial solid solution
  - N also present as nitrides of alloying metals
  - C also present as metal carbides
  - carbonitrides maybe also form
- ^{14}C is potentially present in Zircaloy / stainless steel **after** irradiation as
  - interstitial ^{14}C from interstitial N
  - carbides / carbonitrides
- Corrosion leads to formation of volatile and/or dissolved compounds
  - hydrocarbons/CO (carbonates from oxides)
- Chemical state of ^{14}C is far from clear in Zircaloy / stainless steel / spent nuclear fuel

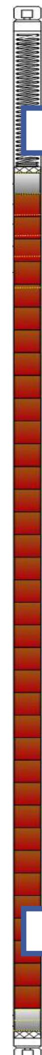
LWR fuel assembly parts

Gösgen (CH) PWR core:

- 177 fuel assemblies
- 15×15 lattice
    - 205 fuel rods
    - 20 guide tubes

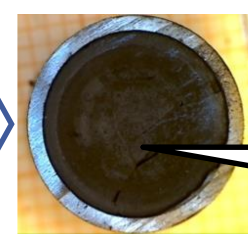






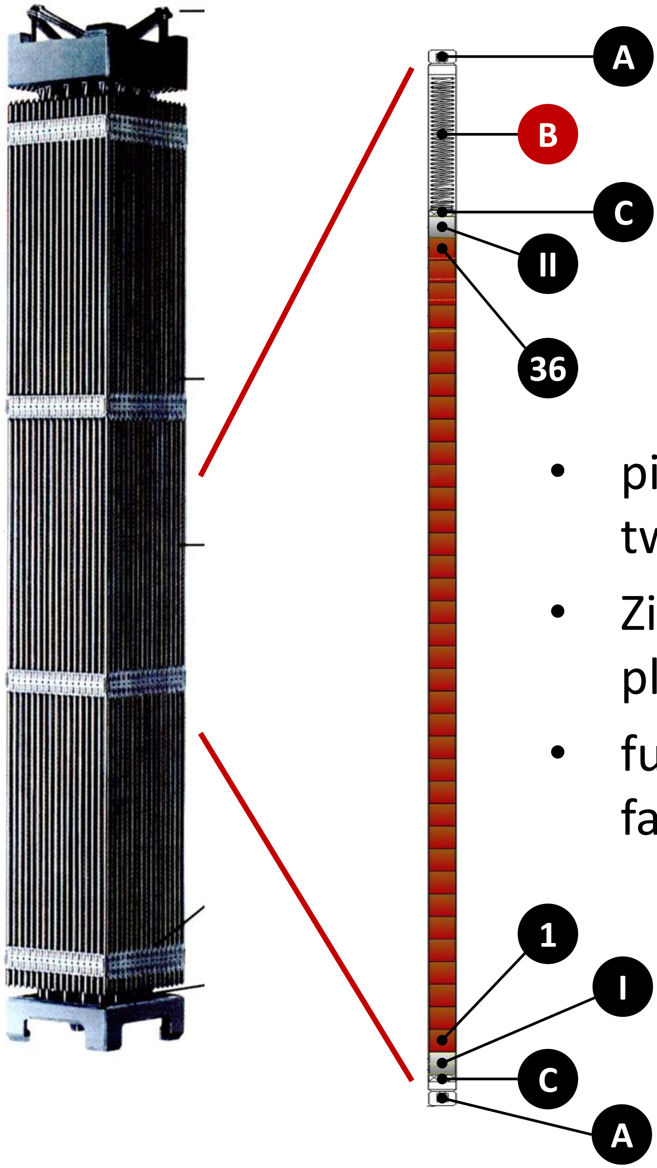
^{60}Co
^{55}Fe
^{63}Ni
^{59}Ni
^{14}C

^{60}Co
^{125}Sb
^{55}Fe
^{14}C
^{137}Cs
^{90}Sr



An (Pu, Np, Am,…)
FP (^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I,…)
AP (**^{14}C**)

Origin of the material used in this study



B **Zircaloy-4 cladding around stainless steel spring**

no contamination of cladding by fuel

- pin KKG–SBS1108 consists of five fuel rod segments + two dummy segments
- Zircaloy-4 cladding specimen are sampled from the plenum of fuel rod segment SBS1108–N0204
- fuel rod segment with UO_2 fuel pellets (3.8 wt.% ^{235}U), fabricated by "Kraftwerk Union AG" (today Areva)

A **end cap**

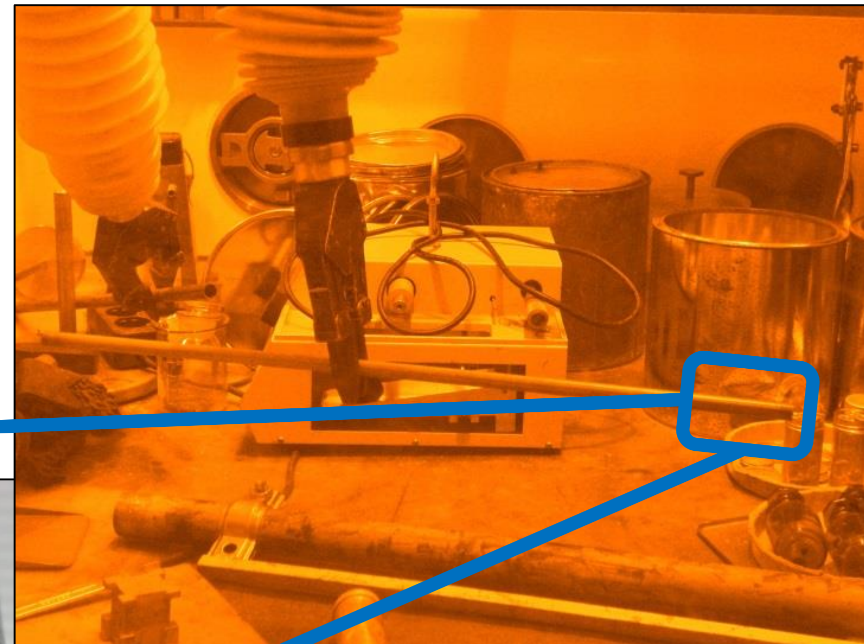
C **insulation pellet**

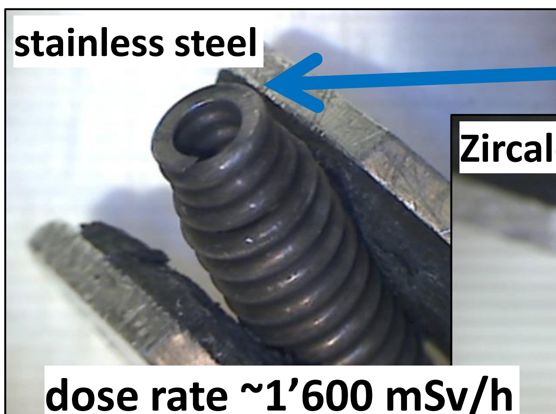
I + **II** **"natural" UO_2**

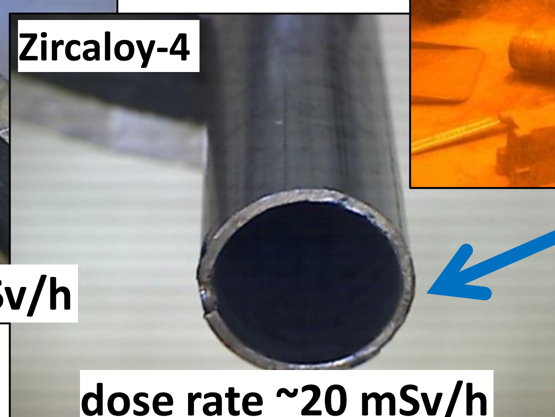
1 … **36** **"enriched" UO_2**

Irradiation characteristics of SBS1108

- Irradiated in the Swiss Gösgen PWR during four cycles (1985–1989)
- 1226 effective full power days
- Average burn-up: 50.4 GWd/t_{HM}
- Average linear power: 260 W/cm
- Max *T*: > 1300°C
- Stored gas tight until 2012

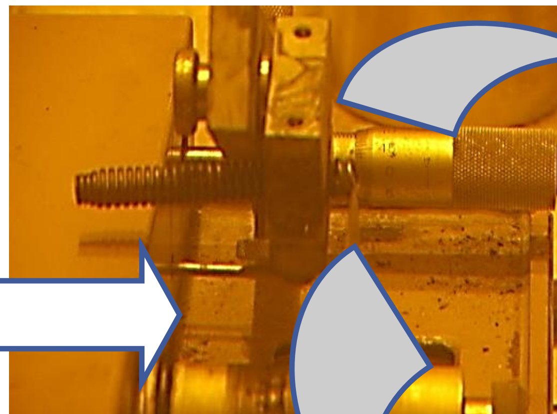


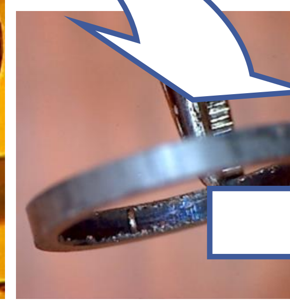




Preparation of subsamples

- Preparation of small subsamples by dry cutting in hot cell





dissolution experiments in glove box

dose rate ≤ 0.3 mSv/h

dissolution experiments in hot cell

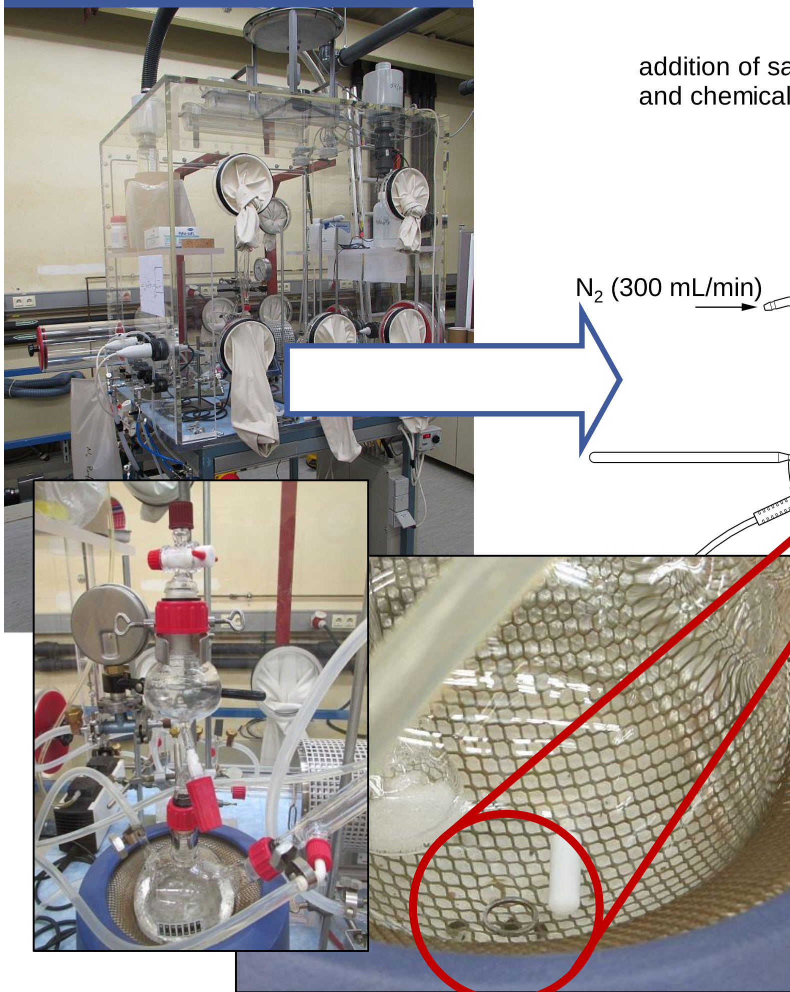
dose rate ≤ 120 mSv/h

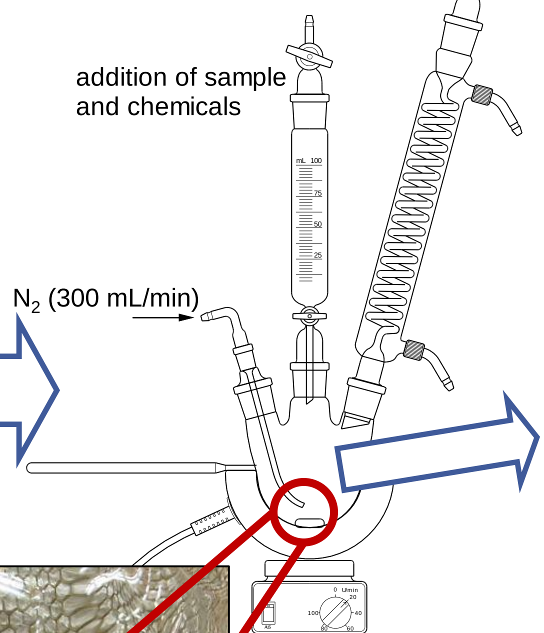
	Zircaloy-4	stainless steel
# of subsamples	6	1
mass [mg]	≤ 189.0	283.0
dose rate [mSv/h]	≤ 0.3	≤ 120

Dissolution experiments in glass reactor

dissolution of Zircaloy-4 subsamples in **glove box** using a **flask**

^{14}C extraction glove





to ^{14}C extraction system

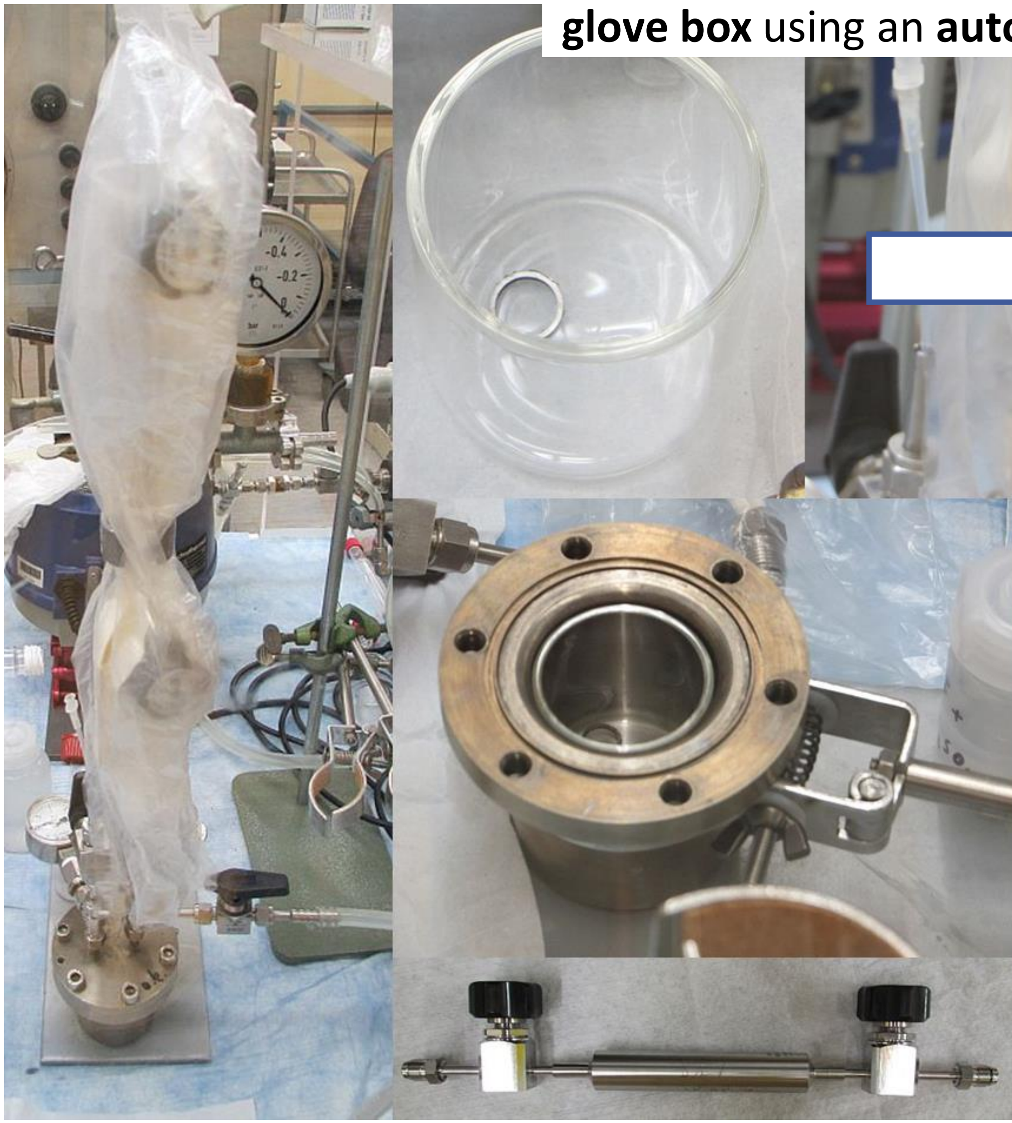
Liquid scintillation counting (LSC) for [^{14}C]

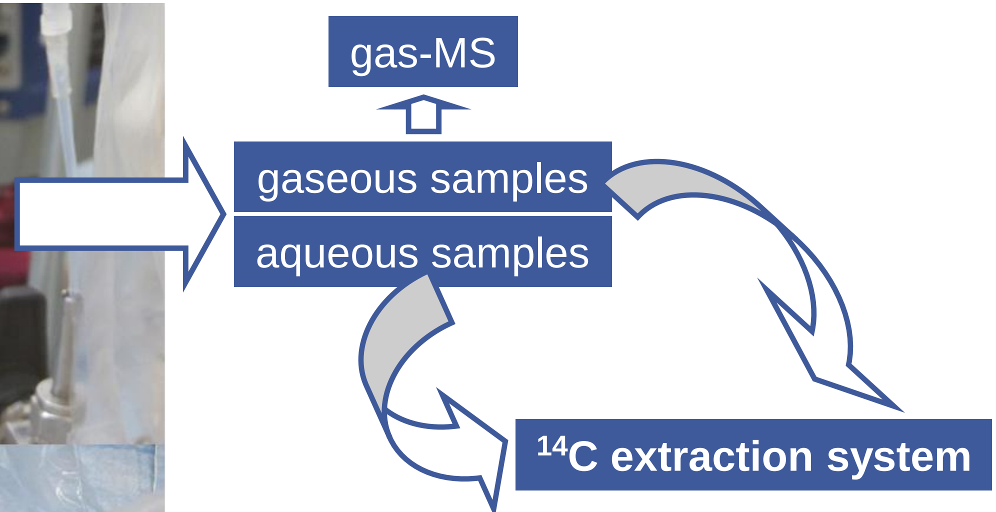
conventional (radio)chemical analyses determining e.g. ^{60}Co, ^{125}Sb, ^{137}Cs, actinides

- cladding sample is placed in a flask
- 100 mL 24% H_2SO_4 added
- 50 mL 10% HF added
- cladding digested within 30 min at RT

Dissolution experiments in autoclave

dissolution of Zircaloy-4 subsamples in **glove box** using an **autoclave**



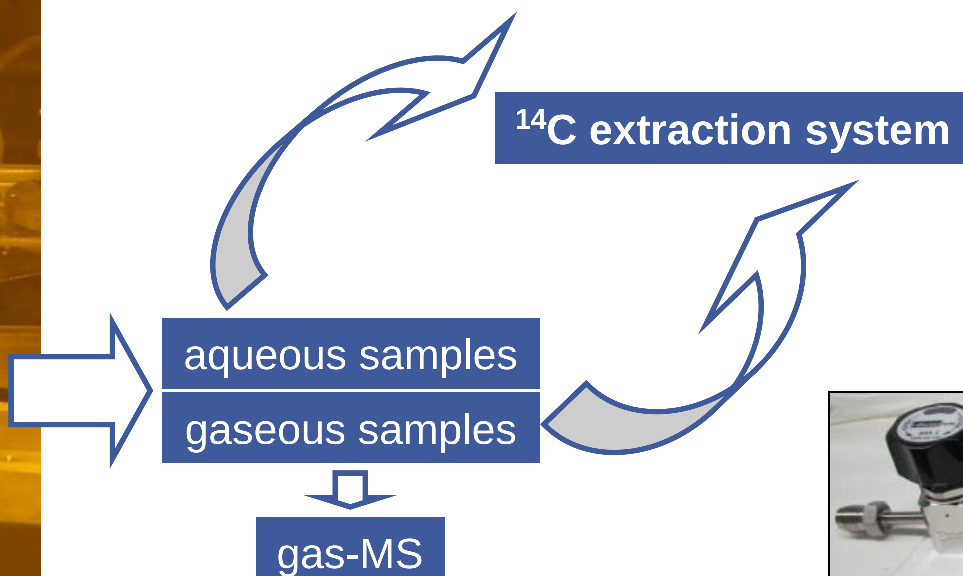


- cladding sample placed in autoclave
- autoclave sealed air tight
- gas collecting cylinder mounted on top
- flushing with Ar or N_2
- 20 mL 16% H_2SO_4 + 3% HF added
- p(autoclave) ~ 1.4 bar

Dissolution experiments in autoclave

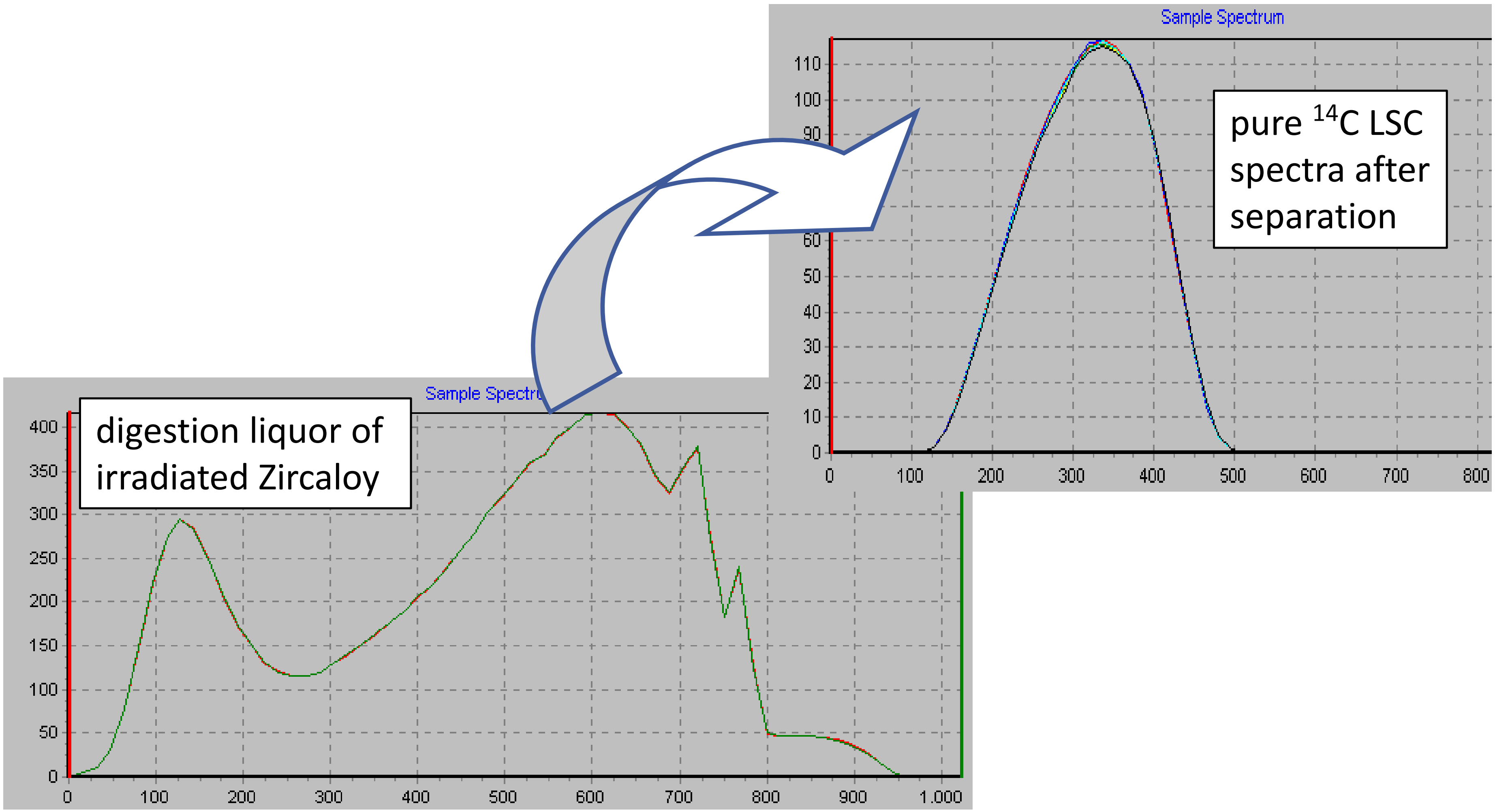
dissolution of stainless steel subsample
in **hot cell** using an **autoclave**

- stainless steel subsample placed in autoclave
- autoclave sealed air tight
- gas collecting cylinder mounted on top
- flushing with Ar
- 150 mL 24% H_2SO_4 + 3% HF added
- digestion of steel sample within a day at RT



Extraction of ^{14}C from digestion liquor

- ^{14}C is a difficult radionuclide to measure: pure soft β^{-} emitter (no γ-rays)



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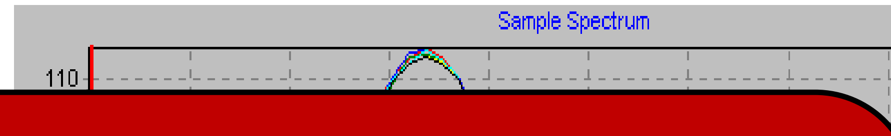
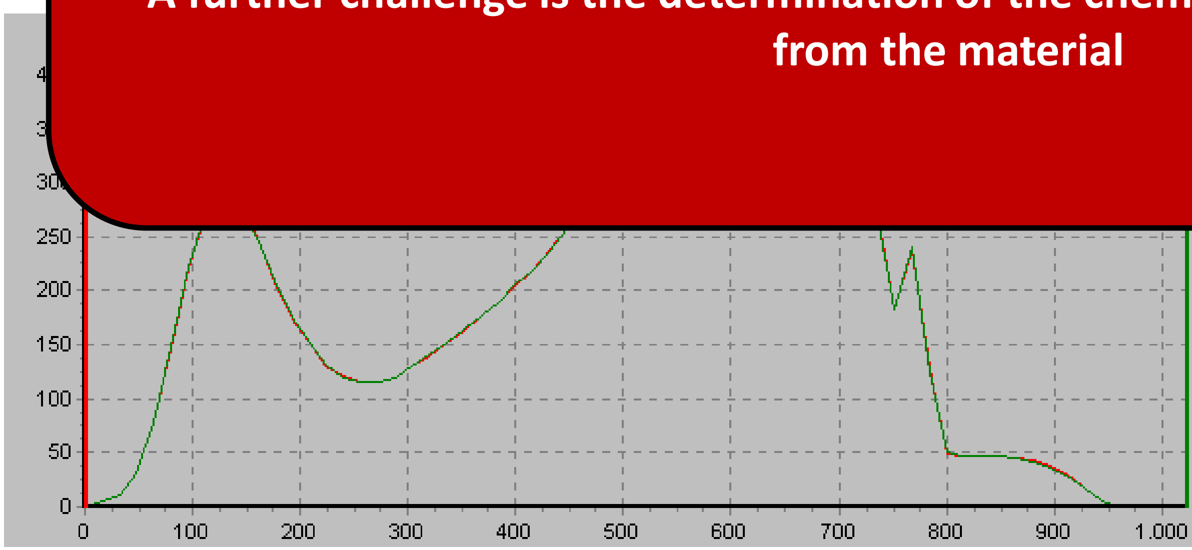


The challenge is a quantitative separation of ^{14}C from other radionuclides present in the aqueous (and gaseous) phase for determining the ^{14}C inventory.

A further challenge is the determination of the chemical form of ^{14}C after release from the material



^{14}C extraction – literature

- Aittola and Olsson (1980)
- Speranzini and Buckley (1981)
- Nott (1982)
- Bleier et al. (1983, 1984, 1987, 1988)
- Salonen and Snellman (1981, 1982, 1985)
- Martin et al. (1986, 1993)
- Moir et al. (1994)
- Stroes-Gascoyne et al. (1994)
- Vance et al. (1995)
- Yamaguchi et al. (1999)
- Magnusson et al. (2005, 2008)
- Schumann et al. (2014)

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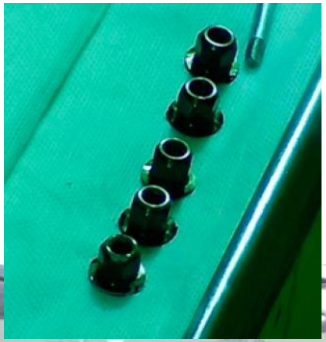
- Martin et al. (1986, 1993)
- Moir et al. (1994)
- **Stroes-Gascoyne et al. (1994)** — **^{14}C inventory in used CANDU fuel**
- Vance et al. (1995)
- **Yamaguchi et al. (1999)** — **^{14}C inventory/chemical form in Zircaloy**
- **Magnusson et al. (2005, 2008)** — **^{14}C chemical form in ion exchange resin**
- **Schumann et al. (2014)** — **^{14}C inventory in stainless steel**

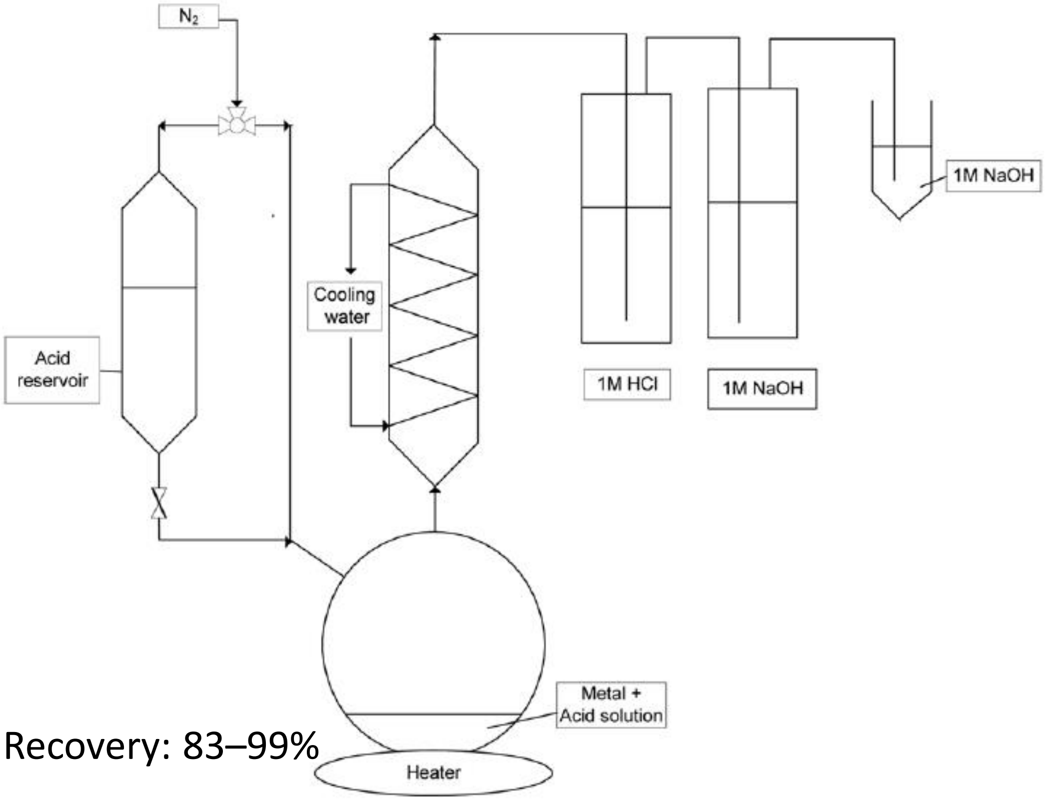
Similarities of methods:

- use of flasks and washing bottles
- alkaline traps → $^{14}CO_2$
- acidic traps → ^{3}H
- furnace (CO, CH_4 → CO_2)
- acid stripping/digestion
- wet oxidation
- carrier gas (N_2)
- vacuum pump
- Liquid scintillation counting

Schumann et al. (2014)

- Fuel assembly guide tube nuts (stainless steel) irradiated in PWR Gösgen (CH)
- Concentrated HNO_3/HCl (aqua regia) + H_2SO_4/$HClO_4$/HNO_3
- ^{14}C inventory determined by liquid scintillation counting (LSC)

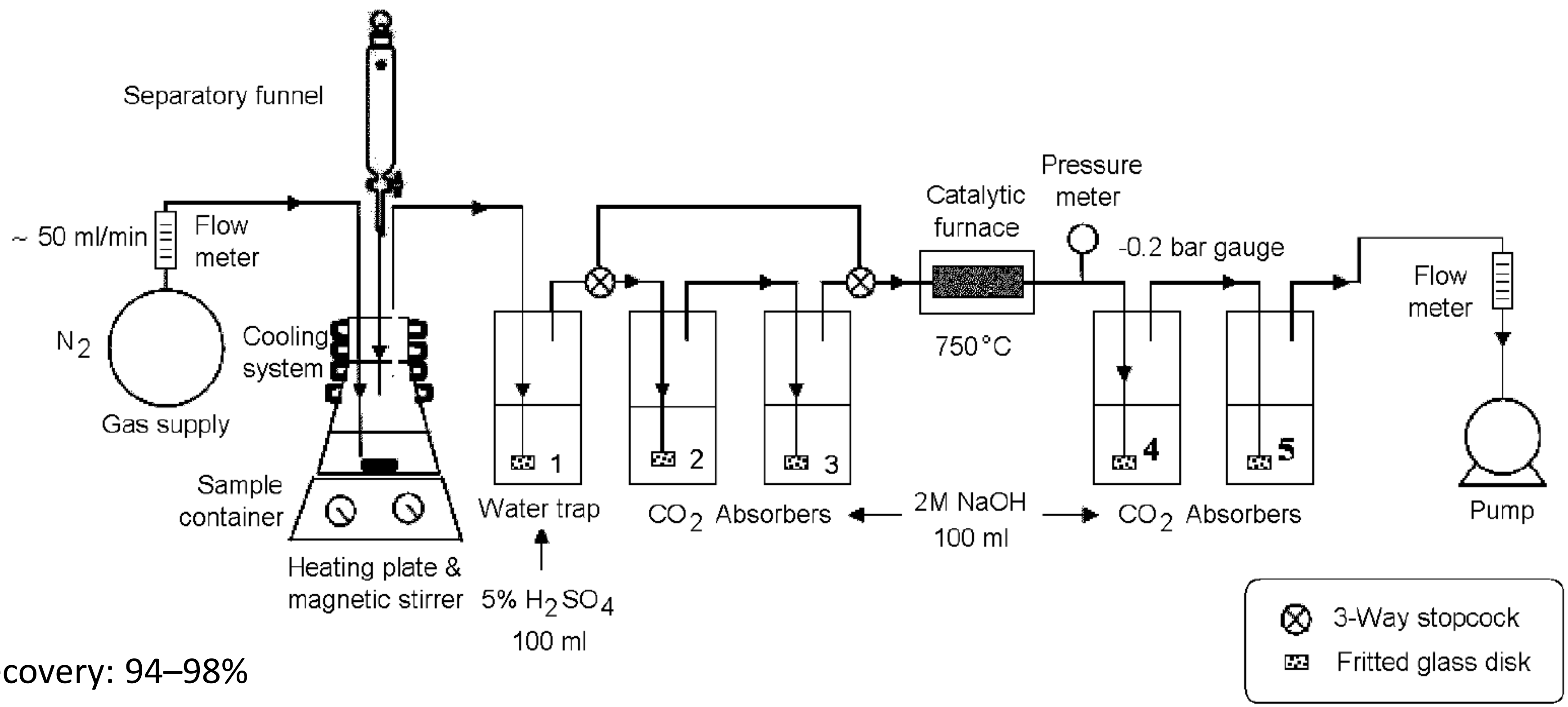




Recovery: 83–99%

Magnusson et al. (2005, 2008)

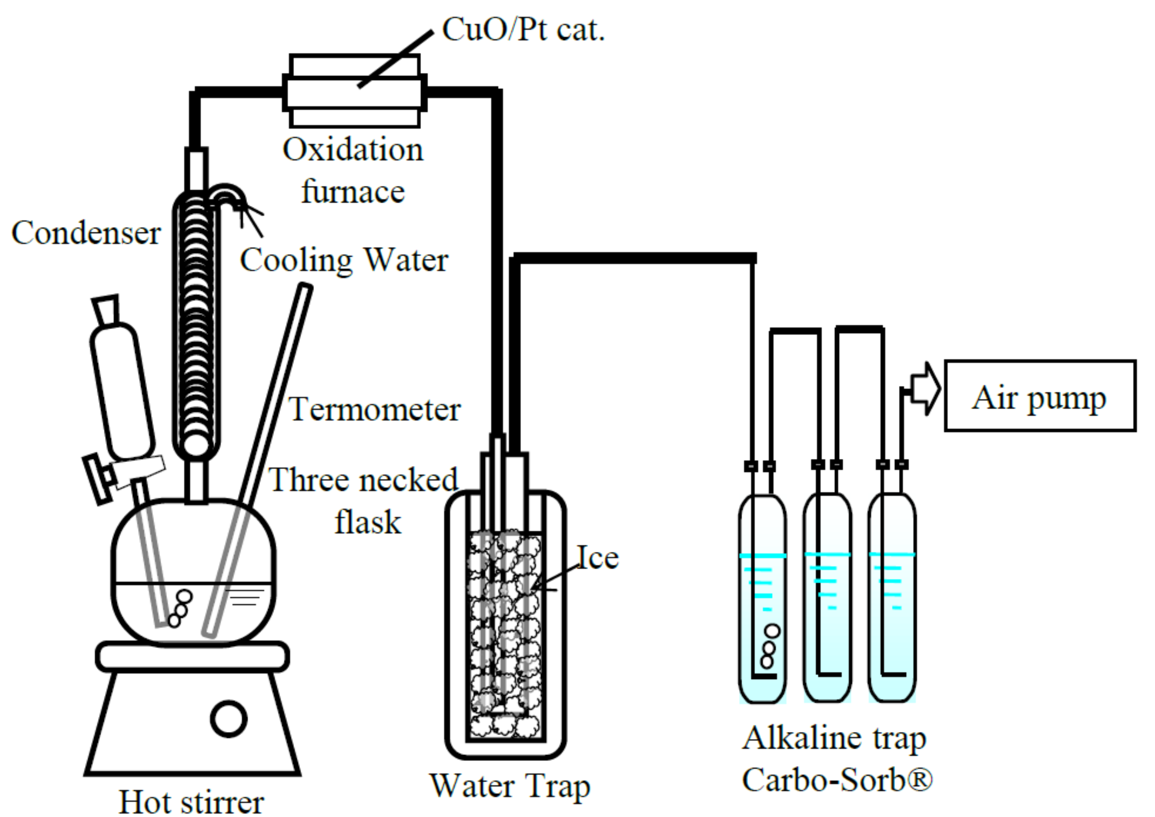
- Spent ion exchange resins and process water from nine PWR and BWR (Sweden)
- 6/8 M H_2SO_4 (acid stripping) + $K_2S_2O_8/AgNO_3$ (wet oxidation)
- ^{14}C inventory and chemical form determined in washing bottles using LSC



Recovery: 94–98%

Yamaguchi et al. (1999)

- Zircaloy-4 with/without oxide layer irradiated in PWR (47.9 GWd/t_{HM})
- HNO_3 + HF
- ^{14}C inventory determined in washing bottles (chemical form of ^{14}C determined in leaching experiments)



Recovery: 80–100%

Stroes-Gascoyne et al. (1994)

- Used CANDU fuels (5.4–15.5 GWd/t_{HM}), one pellet of about 20 g
- Boiled in 50% HNO_3 + 1.6 M $Na_2S_2O_8$, 6 h under refluxing
- ^{14}C inventory determined by LSC

Experimental set-up:

- Flask with cooler and washing bottles
- N_2 as carrier gas
- ^{3}H trap (0.1 M HNO_3)
- ^{14}C trap (0.2 M NaOH)
- furnace (CuO, 500°C)
- activated charcoal filter to remove ^{129}I

Recovery: 87.6 ± 11.9%

^{14}C extraction set-up and procedure

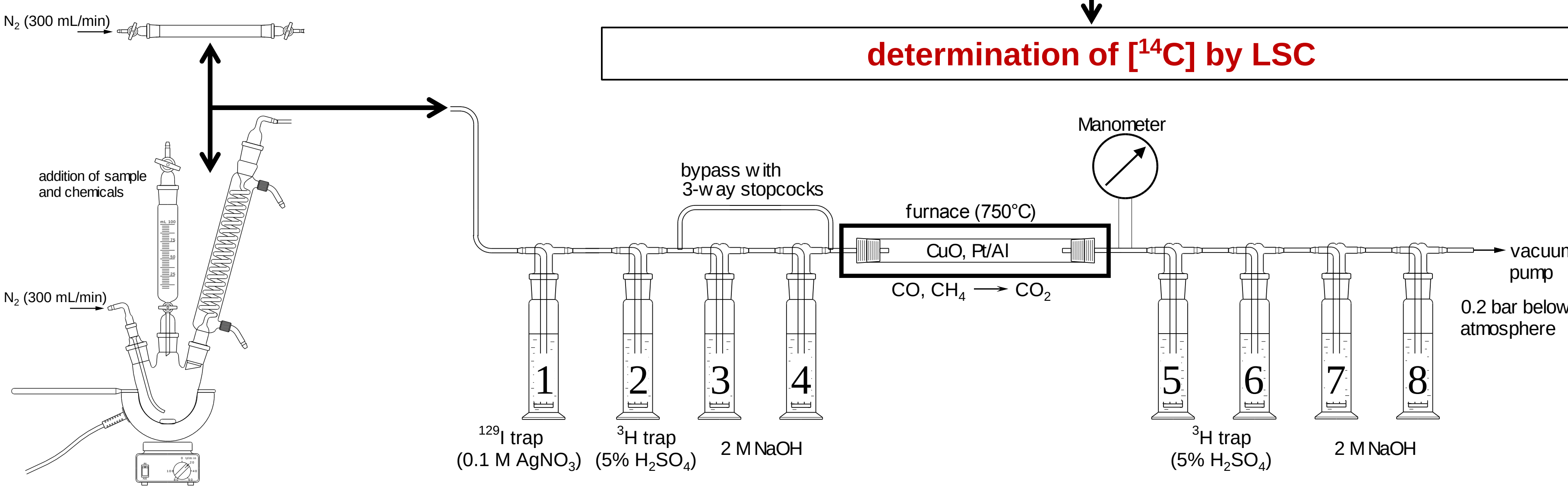
acid digestion in glass reactor

acid digestion in autoclave

gas-MS

absorption of $^{14}CO_2/CO_2$ in various washing bottles

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

→ **gas-MS**

gases released during digestion / gaseous samples

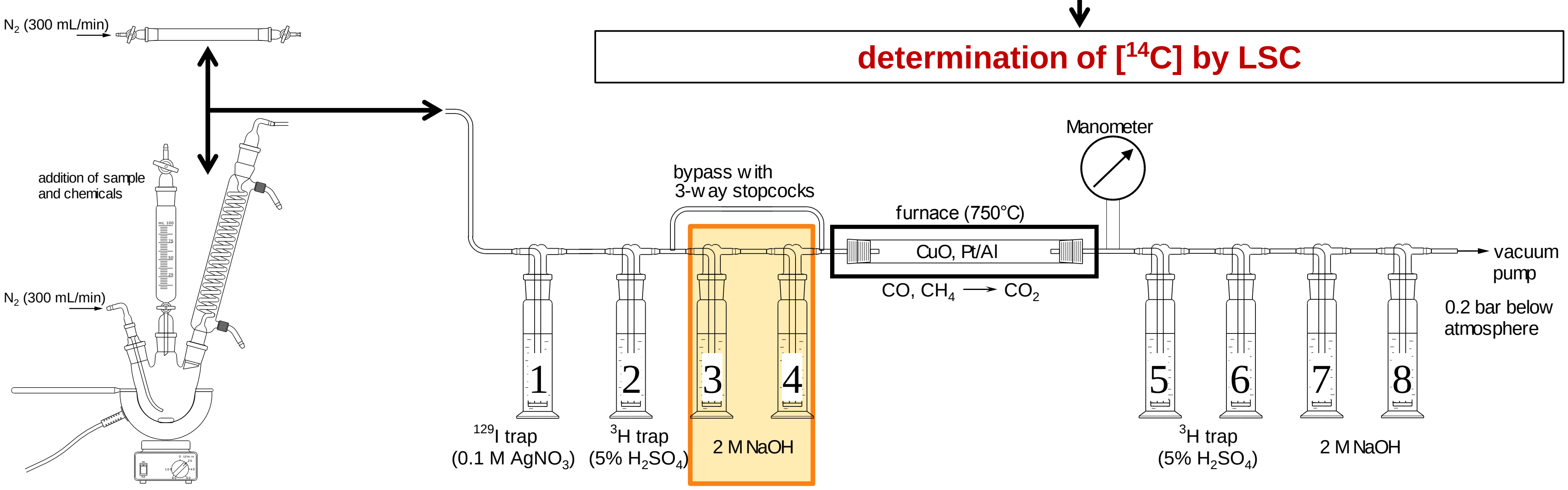
CO_2

↓

absorption of $^{14}CO_2/CO_2$ in various washing bottles

↓

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

→ **gas-MS**

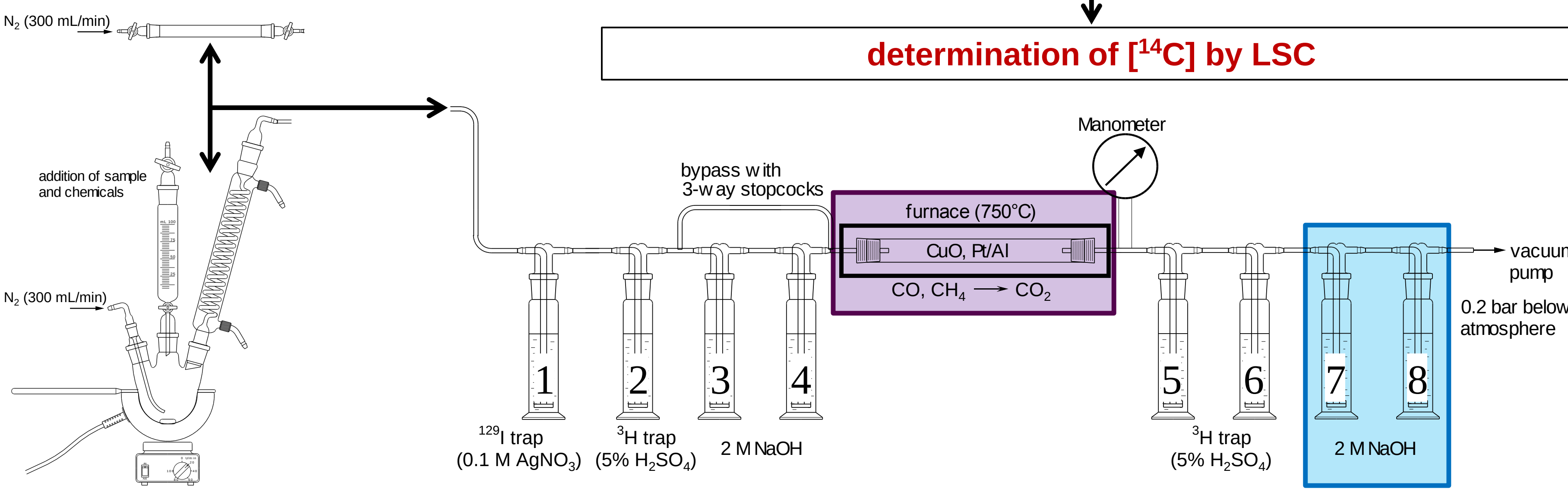
gases released during digestion / gaseous samples

CO, gaseous hydrocarbons → catalytic furnace (CuO, Pt/Al, 750°C)

CO_2

absorption of $^{14}CO_2/CO_2$ in various washing bottles

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

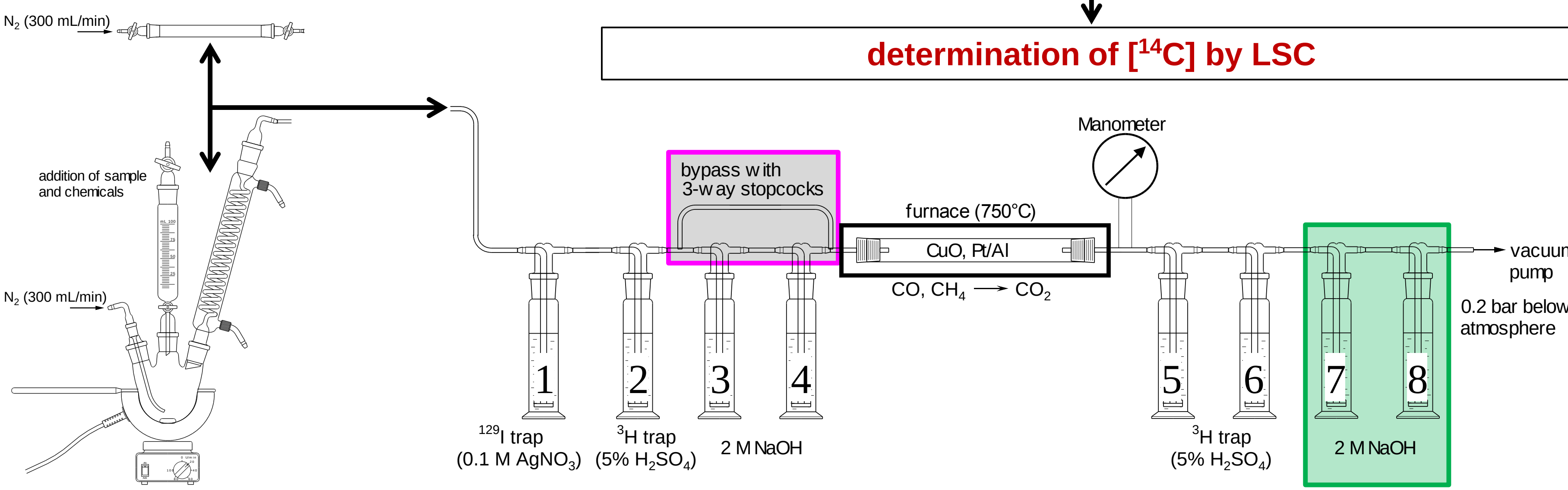
→ gas-MS

gases released during digestion / gaseous samples		acidic digestion liquor
CO, gaseous hydrocarbons	CO_2	dissolved hydrocarbons
↓ catalytic furnace (CuO, Pt/Al, 750°C)	↓	↓ wet oxidation ($K_2S_2O_8$, $AgNO_3$, 95°C)

absorption of $^{14}CO_2/CO_2$ in various washing bottles

↓

determination of [^{14}C] by LSC



^{14}C extraction set-up and procedure

acid digestion in glass reactor

acid digestion in autoclave

→ **gas-MS**

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absorption of $^{14}CO_2/CO_2$ in various washing bottles

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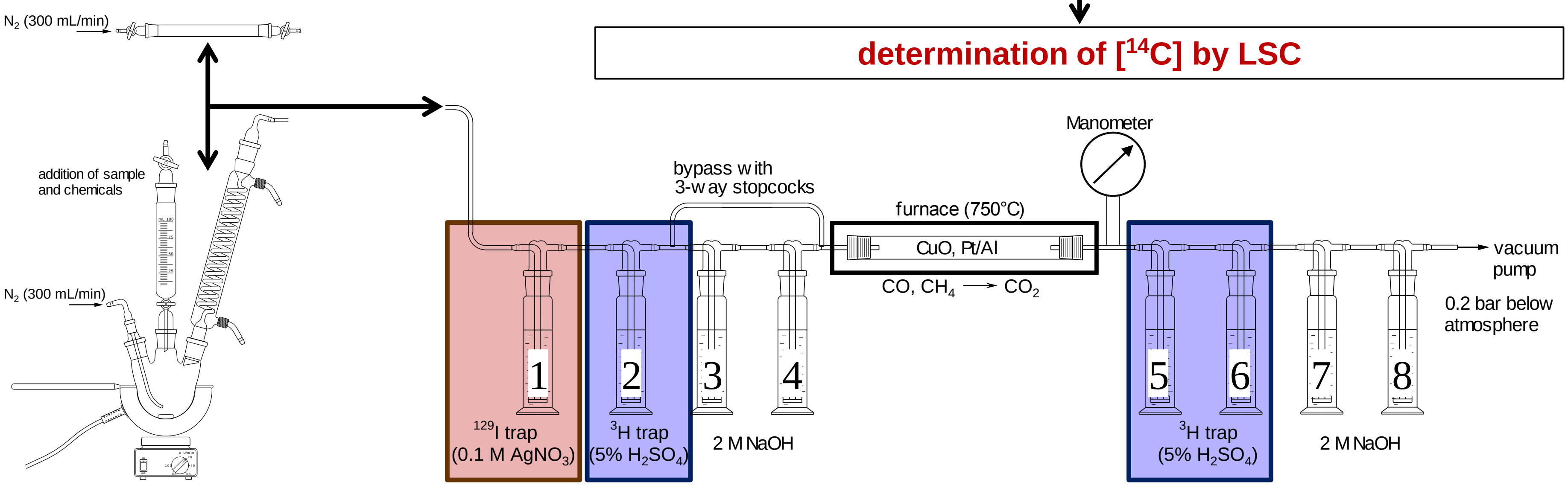
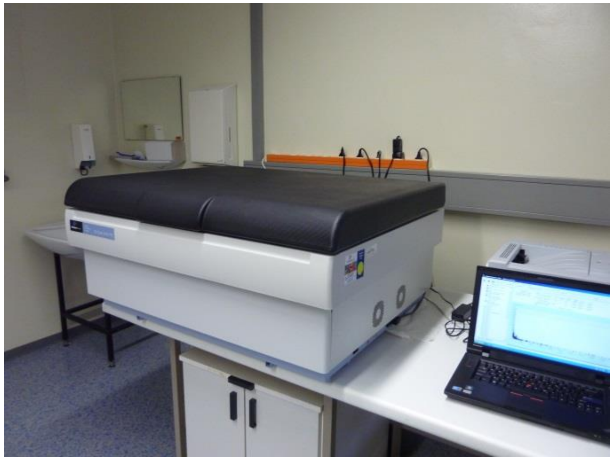


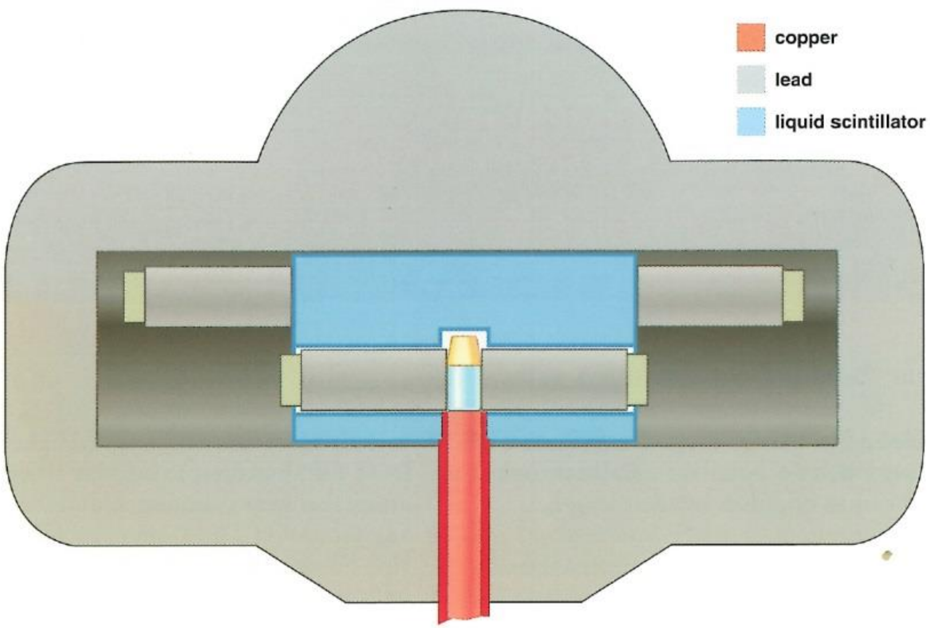
Methods: LSC measurements

- Determining activity of a radioactive sample by mixing the active material with a liquid scintillation cocktail (Toluene, Xylene)
- Radiation emitted by radionuclides transfers energy to solvent molecules
- Excited molecules relax back to ground state by emitting photons
- Photomultiplier converts and multiply light quanta into electrons which are subsequently detected by a semiconductor detector
- Detected light quanta are directly proportional to the decay energy




Methods: LSC measurements

- ultra-low level LSC spectrometer (Quantulus 1220, Wallac Oy, PerkinElmer)
- passive shielding (lead)
- active guard technology (active shielding)
  → remove natural background fluctuations by an anti-coincidence guard counter that detects cosmic and environmental γ radiation

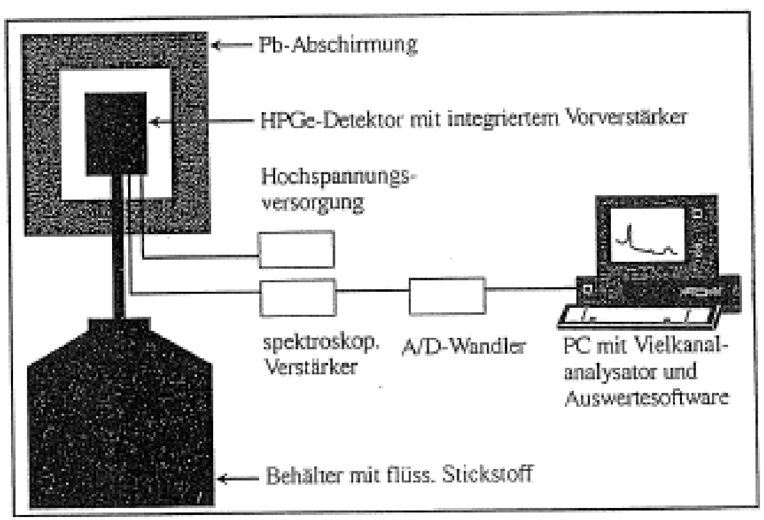


Methods: LSC measurements

- Polyvials used for counting (20 mL, PE, Zinsser Analytic)
- ^{14}C:
  - 3 mL sample solution (NaOH, collected from washing bottles #3, #4, #7, #8)
  - mixed with 18 mL scintillation cocktail (Hionic Fluor, PerkinElmer)
  - measuring time: 3 × 30 min
- ^{55}Fe:
  - separated from other radionuclides present in the digestion liquor by extraction column
  - 1 mL sample (1.5 M HCl) mixed with 10 mL scintillation cocktail (Ultima Gold LLT, PerkinElmer)
  - measuring time: 1 × 30 min

Methods: γ measurements

- Solid-state detectors (semiconductor detectors) e.g. high purity germanium (HPGe) used
- Rely on detection of electron-hole pairs generated by γ-rays in semiconductor material
- Electrons and holes move to respectively charged electrodes due to electric field applied to the detector and create electrical signal



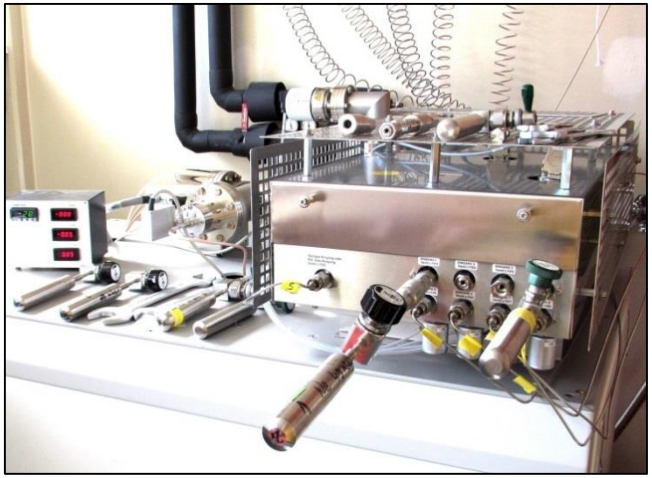
Methods: γ measurements

- Determination of ^{125}Sb and ^{137}Cs
- Extended range coaxial Ge detector (GX3018, Canberra Industries Inc.)
- APEX screw-cap microcentrifuge tubes (2 mL, PP, Alpha Laboratories Ltd.)
- ^{125}Sb and ^{137}Cs:
  - 1 mL aliquot from digestion liquor
  - measuring time: 2–4 h
- ^{125}Sb (after cesium removal to lower background):
  - 2 mL of digestion liquor mixed with 0.1 g AMP*
  - filtration (0.45 µm) of CsAMP suspension
  - 1 mL filtrate used for γ-counting
  - measuring time: 2–4 h

*ammonium molybdophosphate

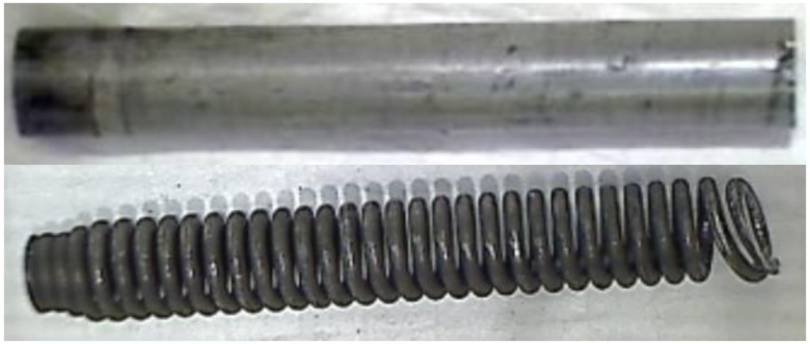
Methods: gas-MS

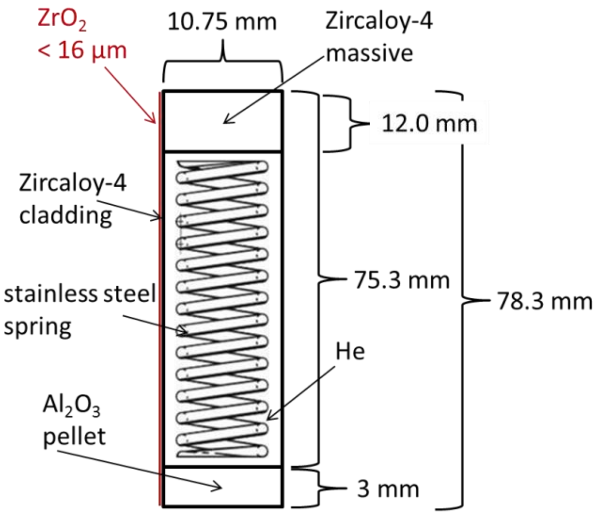
- Analysis for: H_2, N_2, O_2, CO_2, CH_4, Ar,… ([^{14}C-compound] too low for analysis)
- samples are collected in a stainless steel miniature sampling cylinder (V = 50 mL) with two valves (SS-4CS-TW-50, Swagelok)
- quadrupole gas mass spectrometer (GAM400, InProcess Instruments) equipped with secondary electron multiplier (SEM) detector, Faraday cup and batch inlet system
- calibration performed in the same pressure range as samples; 10 measurements are performed with the SEM detector



MCNP inventory calculations

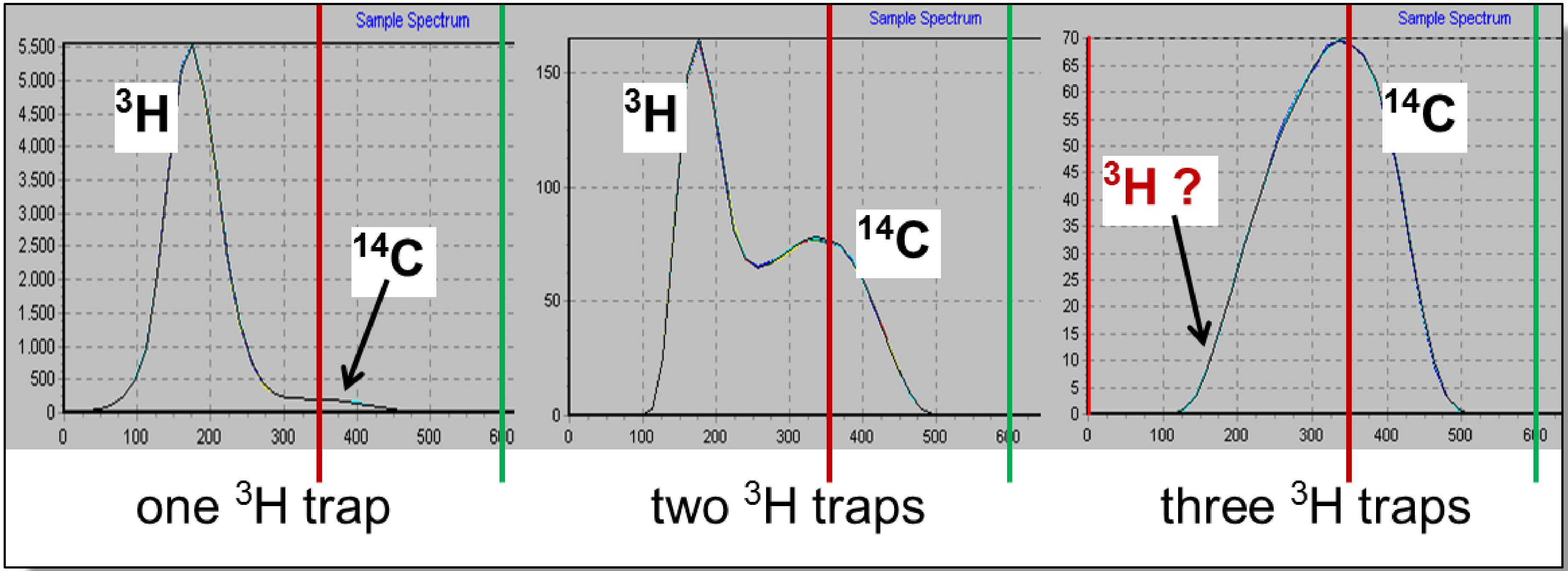
- Calculation of the radionuclide inventory of the irradiated plenum Zircaloy-4 cladding (30 ppm N) and plenum stainless steel spring (80 ppm N)
- Monte Carlo N-Particle transport code (MCNP-X)
  - taking into account nominal composition of unirradiated Zircaloy-4 cladding and stainless steel spring
  - taking into account dimensions, weight and density of the material
  - direct surrounding of the material and (vertical) position in the fuel assembly and nuclear reactor
  - taking into account irradiation characteristics





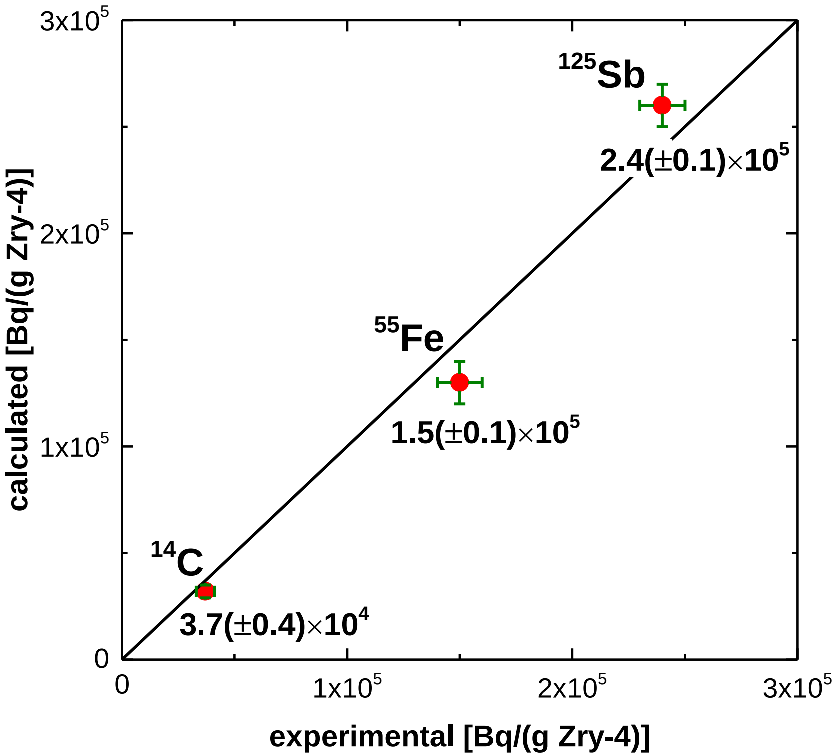
Results – digestion of Zircaloy

- Digestion of irradiated Zircaloy releases quantitatively gaseous ^{1}H–^{3}H (HT)
  → catalytic furnace oxidize HT to HTO, which is absorbed in washing bottles after the furnace



Results – Zircaloy-4

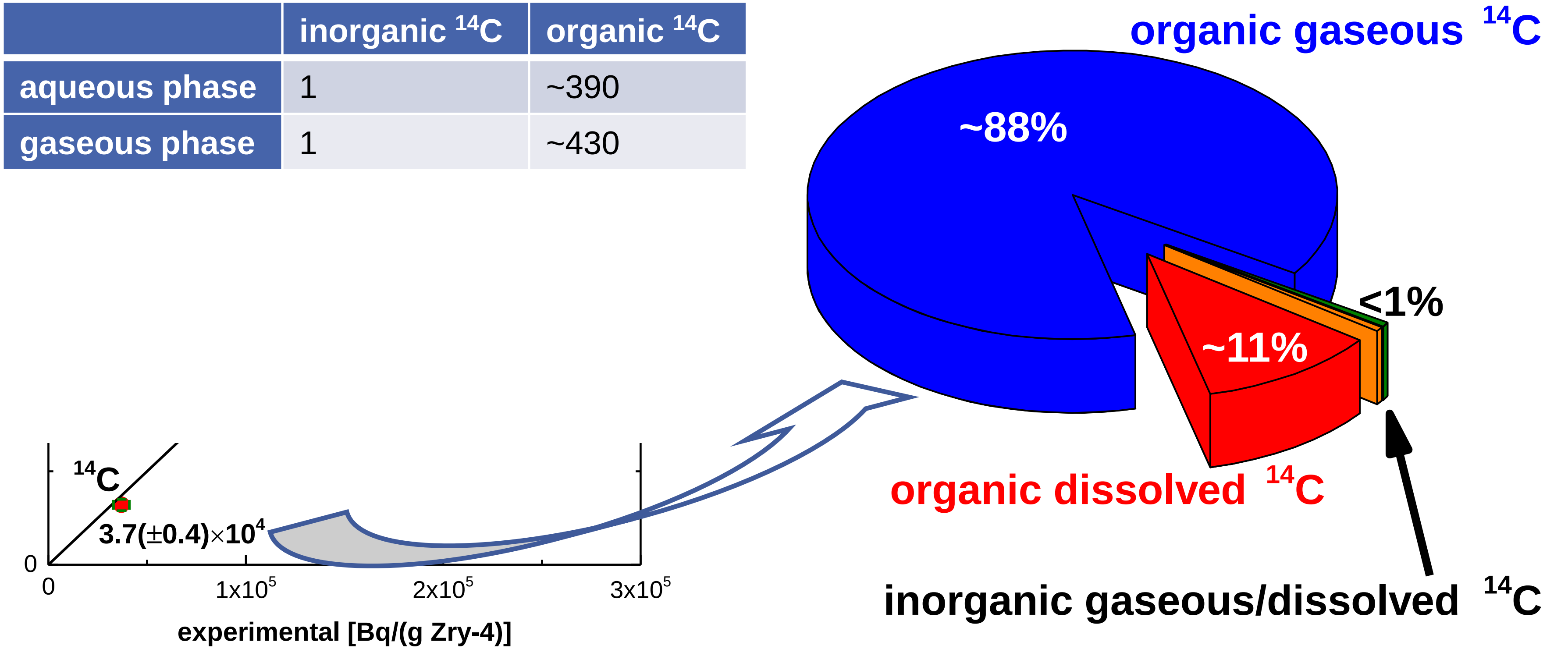
- Experimental and calculated results in good agreement for ^{14}C, ^{55}Fe, ^{125}Sb
- Experimental activities agree, within analytical uncertainty, with calculations
- Experimental ^{137}Cs inventory exceeds calculated by factor 117
  → ^{137}Cs precipitation on inner surface of irradiated Zircaloy cladding



Results – Zircaloy-4

- ~99% of ^{14}C as gaseous/dissolved hydrocarbons or carbon monoxide
- Similar ratio between organic and inorganic ^{14}C bearing compounds in aqueous and gaseous phase

	inorganic ^{14}C	organic ^{14}C
aqueous phase	1	~390
gaseous phase	1	~430

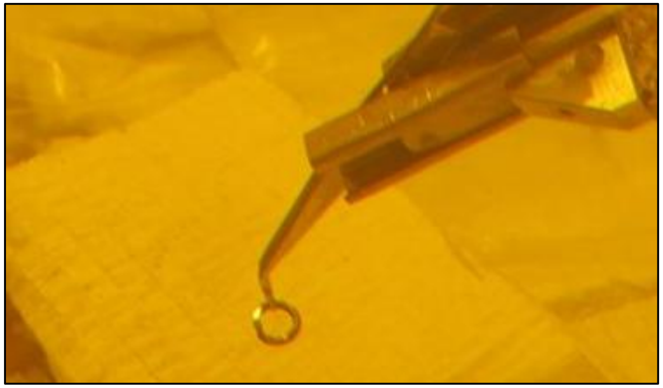


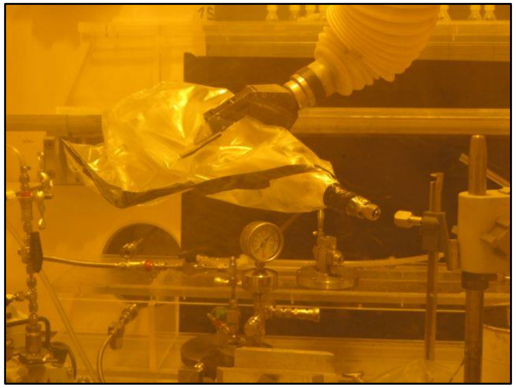
Results – stainless steel

- **Preliminary results:** ^{14}C inventory and chemical form of ^{14}C after release from stainless steel

radionuclide	experimental [Bq/g]	calculated [Bq/g]	factor
^{14}C	$2.7(\pm0.3)\times10^{5}$	$8.5(\pm0.9)\times10^{4}$	3.1

- Experimental and calculated results agree within a factor ~3 for ^{14}C
  → great uncertainty of nitrogen content in stainless steel (0.04–0.1 wt.%)
- ~99% of ^{14}C as gaseous/dissolved hydrocarbons or carbon monoxide





Thank you for your attention!