Ultratrace analysis of radionuclides by AMS

Francesca Quinto

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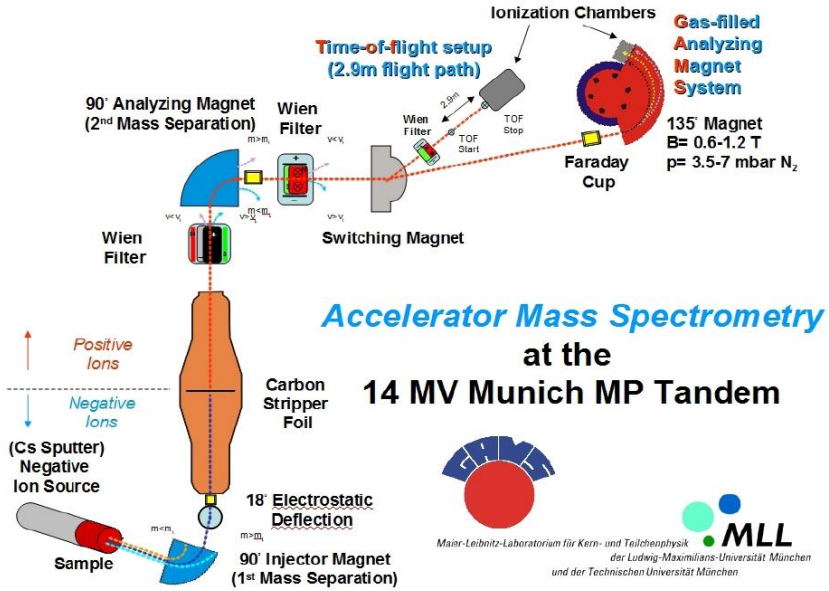
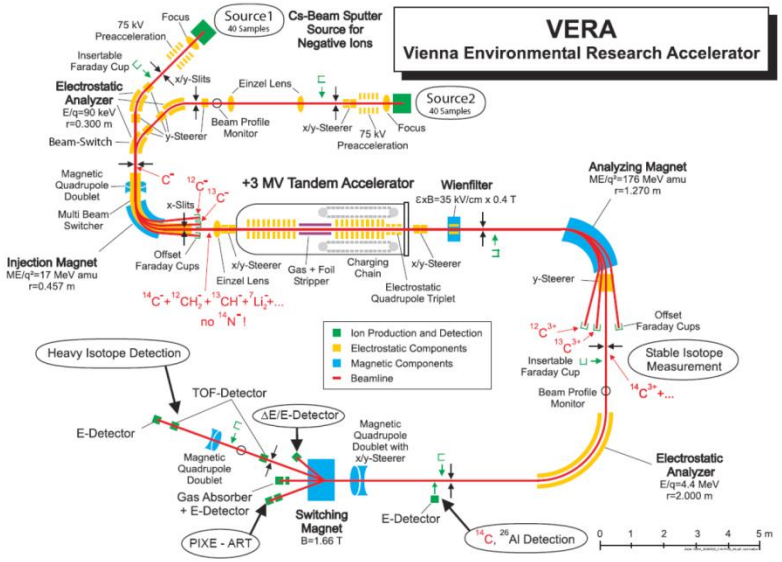
Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposal (KIT-INE)





Outlook

- What is Accelerator Mass Spectrometry (AMS)?
- The most sensitive analytical technique for the investigation of rare long-lived radionuclides in the environment
- Fundaments of AMS
- Different Setups for different nuclides:
  ^{14}C, ^{99}Tc, ^{129}I, ^{236}U, $^{239\text{-}244}Pu$, $^{241,243}Am$, ^{248}Cm
- Fields of Application:

✓ *Archeology*
✓ ***Biomedical research***
✓ ***Environmental science***
✓ *Geology*
✓ ***Monitoring of nuclear contamination***
✓ *Nuclear Physics and Astrophysics*
✓ ***Safety of nuclear waste disposal***

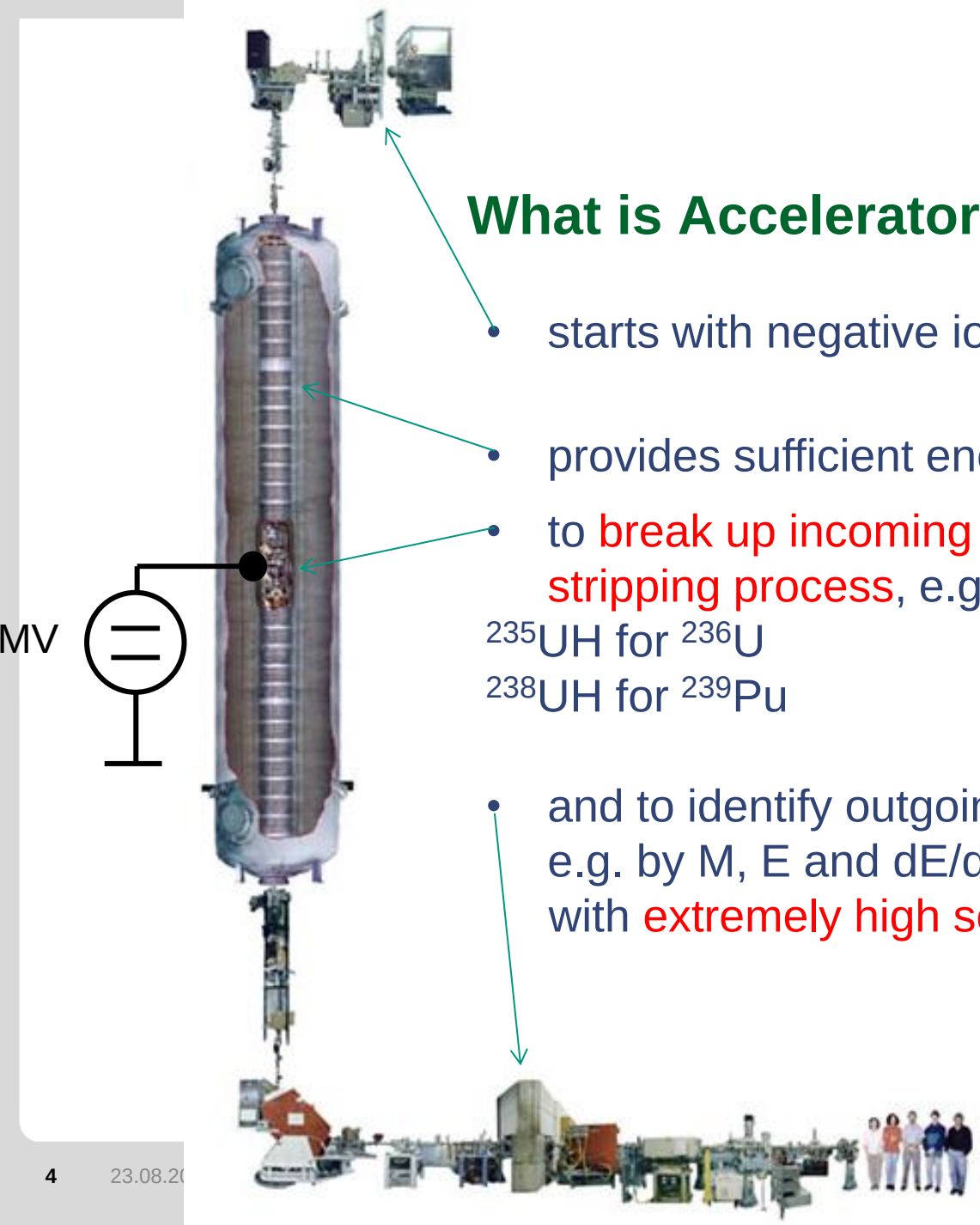
What is Accelerator Mass Spectrometry?

Like in other Mass Spectrometric Techniques:

- Atoms are extracted from a sample and are ionized
- Accelerated to high energies
- Separated according to their momentum, charge and energy
- Individually counted after identification as having correct atomic number and mass

✓ **BUT in AMS the ions are accelerated at MeV by using ion accelerators**

What is Accelerator Mass Spectrometry?

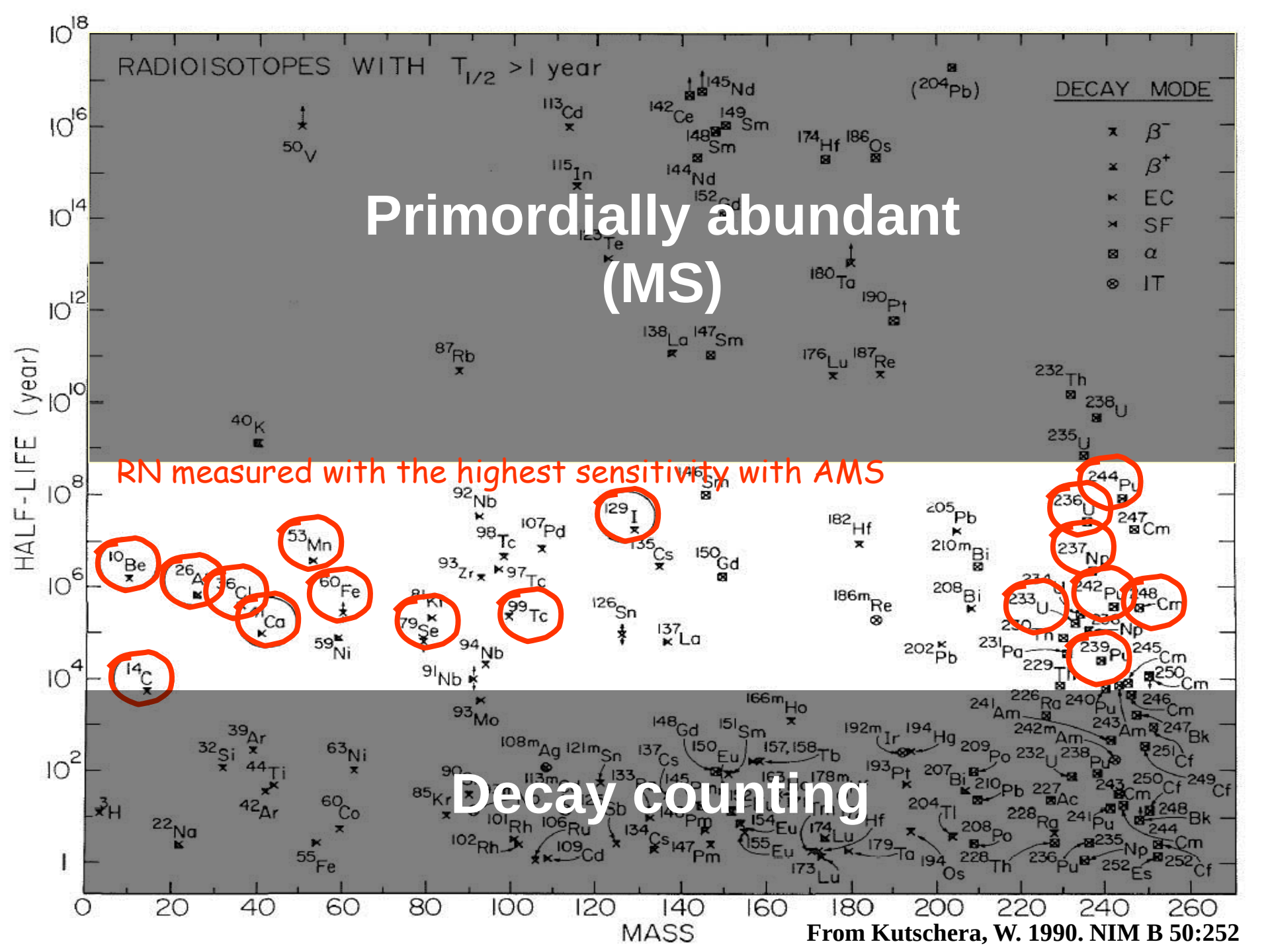


- starts with negative ions and
- provides sufficient energy [MeV]
- to break up incoming molecular ions in the stripping process, e.g. $^{12}CH_2$ and ^{13}CH for ^{14}C

  ^{235}UH for ^{236}U

  ^{238}UH for ^{239}Pu
- and to identify outgoing atomic ions, e.g. by M, E and dE/dx(Z), with extremely high sensitivity

14UD Tandem Accelerator at the Australian National University, Canberra, Australia



From Kutschera, W. 1990. NIM B 50:252

Analytical Capability of AMS

Overall Efficiency:
$^{14}C = 10^{-2}$
$^{129}I = 10^{-3}$
actinide nuclides = 10^{-4}

→ 10^5 atoms of an actinide nuclide (corresponding to tens of attograms) is possible with a 32 % relative uncertainty

A precision of 1%:
10^6 atoms of ^{14}C
10^7 atoms of ^{129}I
10^8 atoms of an actinide nuclide

→ at least 4 and up to 7 orders of magnitude less atoms than a radiometric technique to perform equally precise measurements, with consequent reduction of sample size

abundance sensitivities:
$^{14}C/^{12}C = 10^{-15}$
$^{129}I/^{127}I = 10^{-14}$
$^{236}U/^{238}U = 10^{-13}$

→ unambiguous nuclide detection in environmental samples at concentration levels below ppq

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→ unambiguous nuclide detection in environmental samples at concentration levels below ppq

AMS the most sensitive analytical technique for the investigation of rare long-lived radionuclides in the environment

An example:

1 mg C with a natural $^{14}C/^{12}C = 1.2 \times 10^{-12}$

- **6×10^7 atoms ^{14}C**
- **$t_{1/2}$ = 5700 y**
- **Radiometric method: ca. 1 decay of ^{14}C in one hour = 0.28 mBq (< DL of Liquid Scintillation)**
- **Mass Spectrometry: atom counting**
- **AMS => Isobaric interference are removed:**

✓ **$^{14}N^-$ in the ion source**

✓ **$^{12}CH_2^-$ and $^{13}CH^-$ in the terminal of the accelerator**

- **AMS: 6×10^7 atoms ^{14}C counted with an efficiency of 1% in one hour with a precision ca. 0.1%**

An example:

1 µg C with a natural $^{14}C/^{12}C = 1.2 \times 10^{-12}$

- **6×10^4 atoms ^{14}C**
- **$t_{1/2}$ = 5700 y**
- **Radiometric method: ca. 0.001 decay of ^{14}C in one hour = 0.00028 mBq (<< DL of Liquid Scintillation)**
- **Mass Spectrometry: atom counting**
- **AMS => Isobaric interference are removed:**

✓ **$^{14}N^-$ in the ion source**

✓ **$^{12}CH_2^-$ and $^{13}CH^-$ in the terminal of the accelerator**

- **AMS: 6×10^4 atoms ^{14}C counted with an efficiency of 1% in one hour with a precision of ca. 4%**

Facilities used for AMS

Big

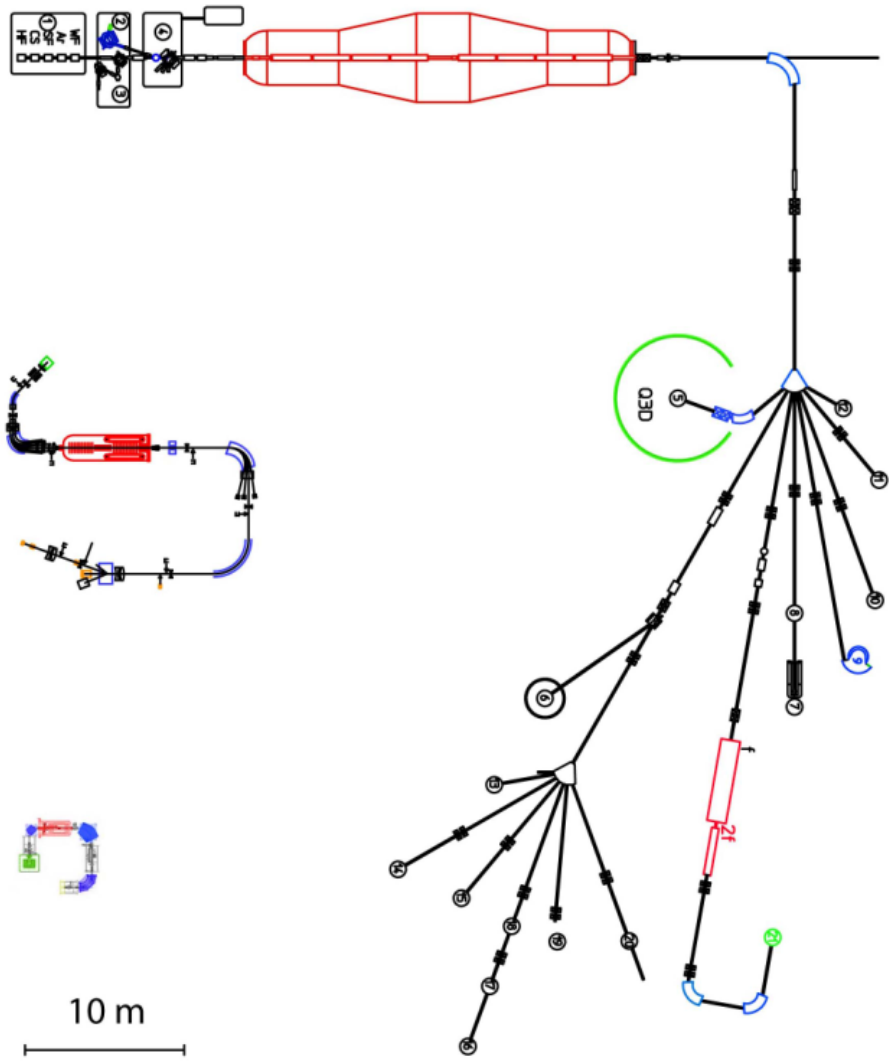
15 MV Tandem
TU and LMU München
Germany

↔

3 MV Tandem VERA
Universität Wien
Austria

Small

0.5 MV Tandem
ETH Zürich
Switzerland



Components of AMS

- ❑ Filtering devices:

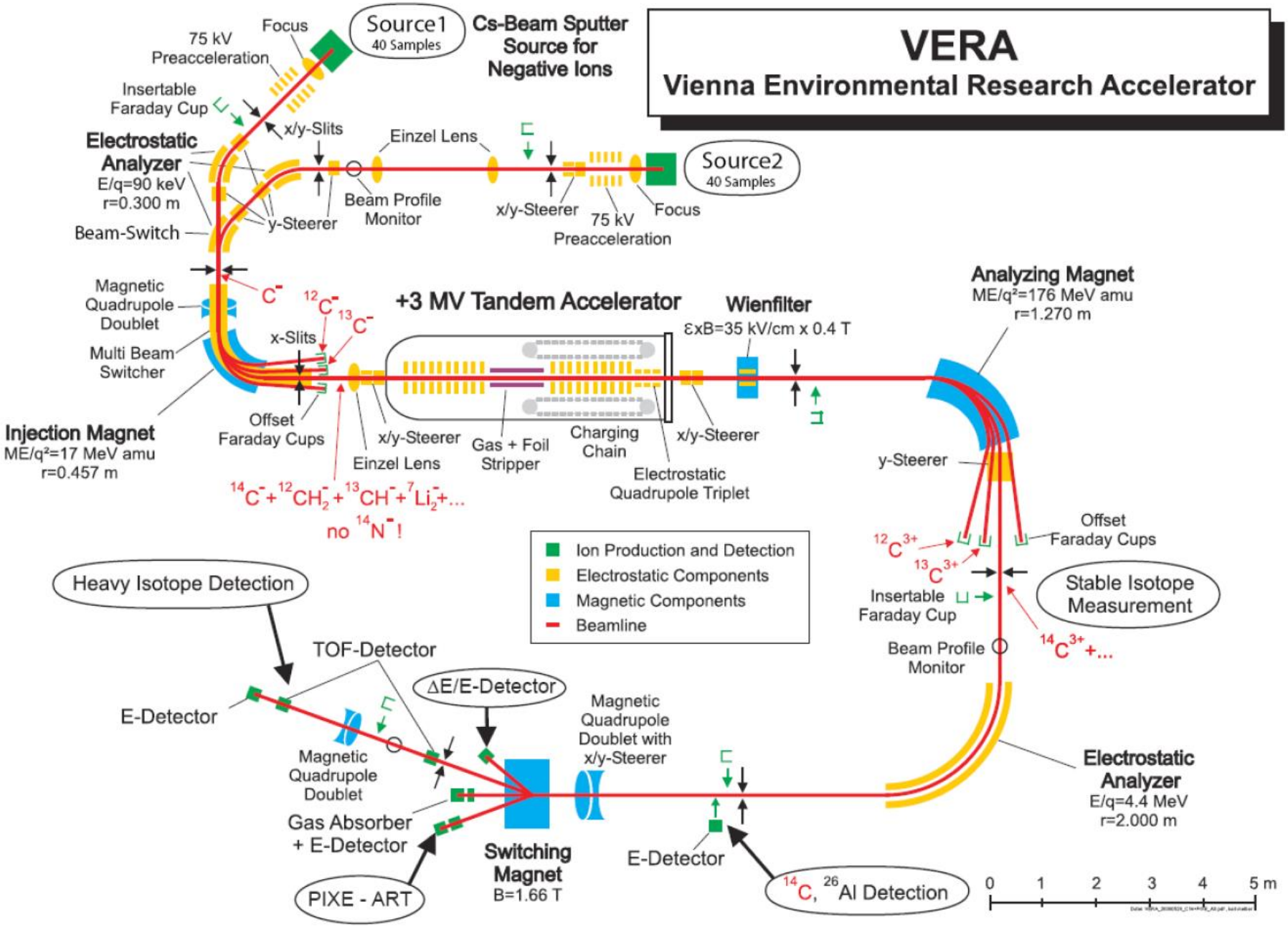
  - Dipole magnets
  - Electrostatic analyzers
  - Wien Filters

- ❑ Devices for the destruction of molecular isobars:

  - Tandem Electrostatic Accelerator

- ❑ Devices for the separation of atomic isobars:

  - For e.g. ^{14}C and ^{129}I in the ion source
  - For e.g., ^{53}Mn, ^{60}Fe and ^{99}Tc in the Gas-filled Magnet Analyzing System


VERA
Vienna Environmental Research Accelerator
Source1
40 Samples
Cs-Beam Sputter Source for Negative Ions
Focus
75 kV Preacceleration
Insertable Faraday Cup
Electrostatic Analyzer
E/q=90 keV
r=0.300 m
Beam-Switch
x/y-Slits
Einzel Lens
Beam Profile Monitor
y-Steerer
x/y-Steerer
75 kV Preacceleration
Focus
Source2
40 Samples
Magnetic Quadrupole Doublet
Multi Beam Switcher
Injection Magnet
ME/q²=17 MeV amu
r=0.457 m
C⁻
12C⁻
13C⁻
x-Slits
Offset Faraday Cups
+3 MV Tandem Accelerator
x/y-Steerer
Einzel Lens
Gas + Foil Stripper
Charging Chain
Electrostatic Quadrupole Triplet
Wienfilter
εxB=35 kV/cm x 0.4 T
Analyzing Magnet
ME/q²=176 MeV amu
r=1.270 m
y-Steerer
14C⁻+12CH2⁻+13CH⁻+7Li2⁻+...
no 14N⁻!
Ion Production and Detection
Electrostatic Components
Magnetic Components
Beamline
12C3+
13C3+
Offset Faraday Cups
Insertable Faraday Cup
Beam Profile Monitor
14C3+...
Stable Isotope Measurement
Heavy Isotope Detection
TOF-Detector
E-Detector
ΔE/E-Detector
Magnetic Quadrupole Doublet
Gas Absorber + E-Detector
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B=1.66 T
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E/q=4.4 MeV
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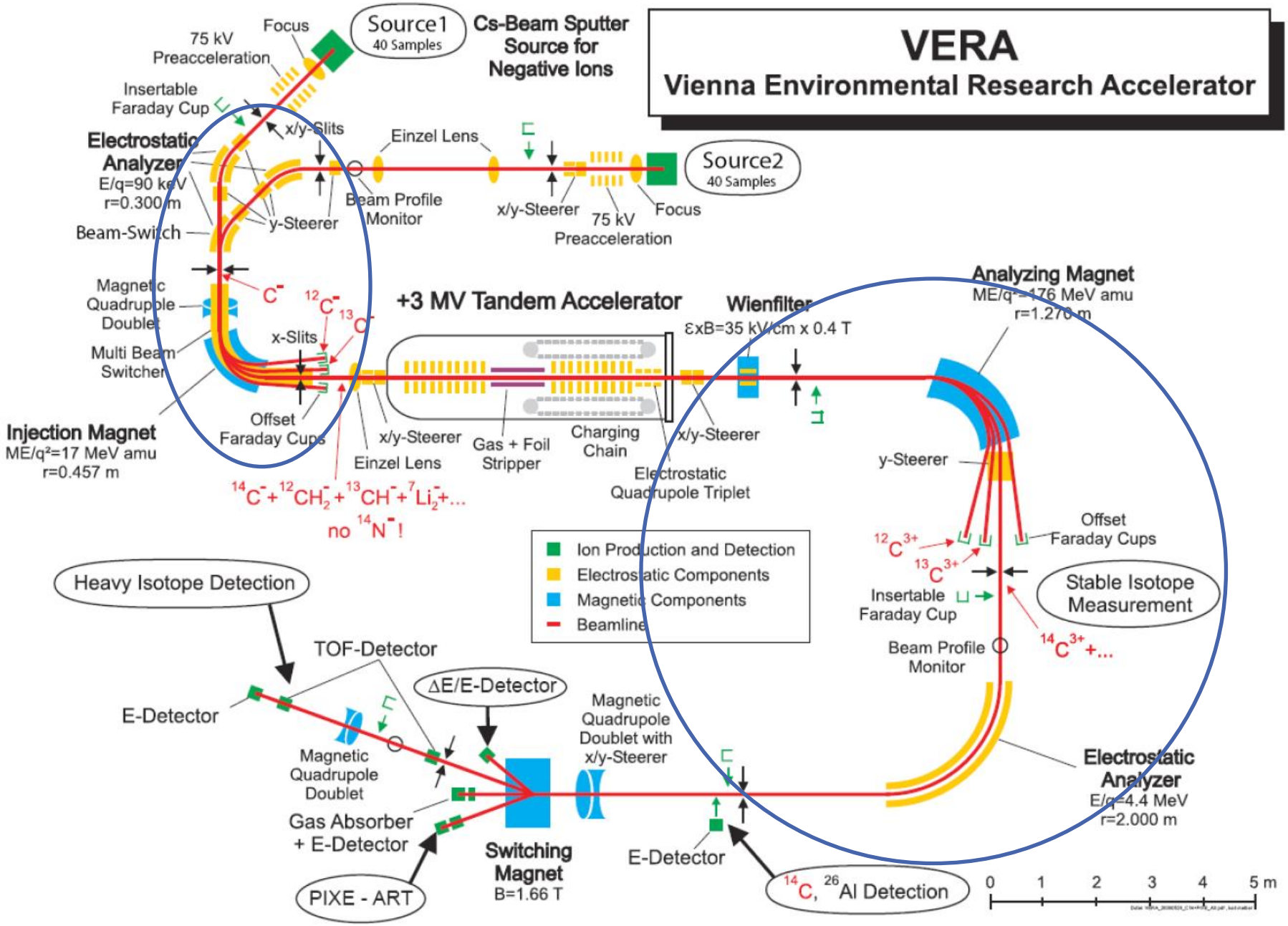
0 1 2 3 4 5 m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Electrostatic Quadrupole Triplet
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14C- + 12CH2- + 13CH- + 7Li2- +...
no 14N- !
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r=2.000 m
0 1 2 3 4 5 m

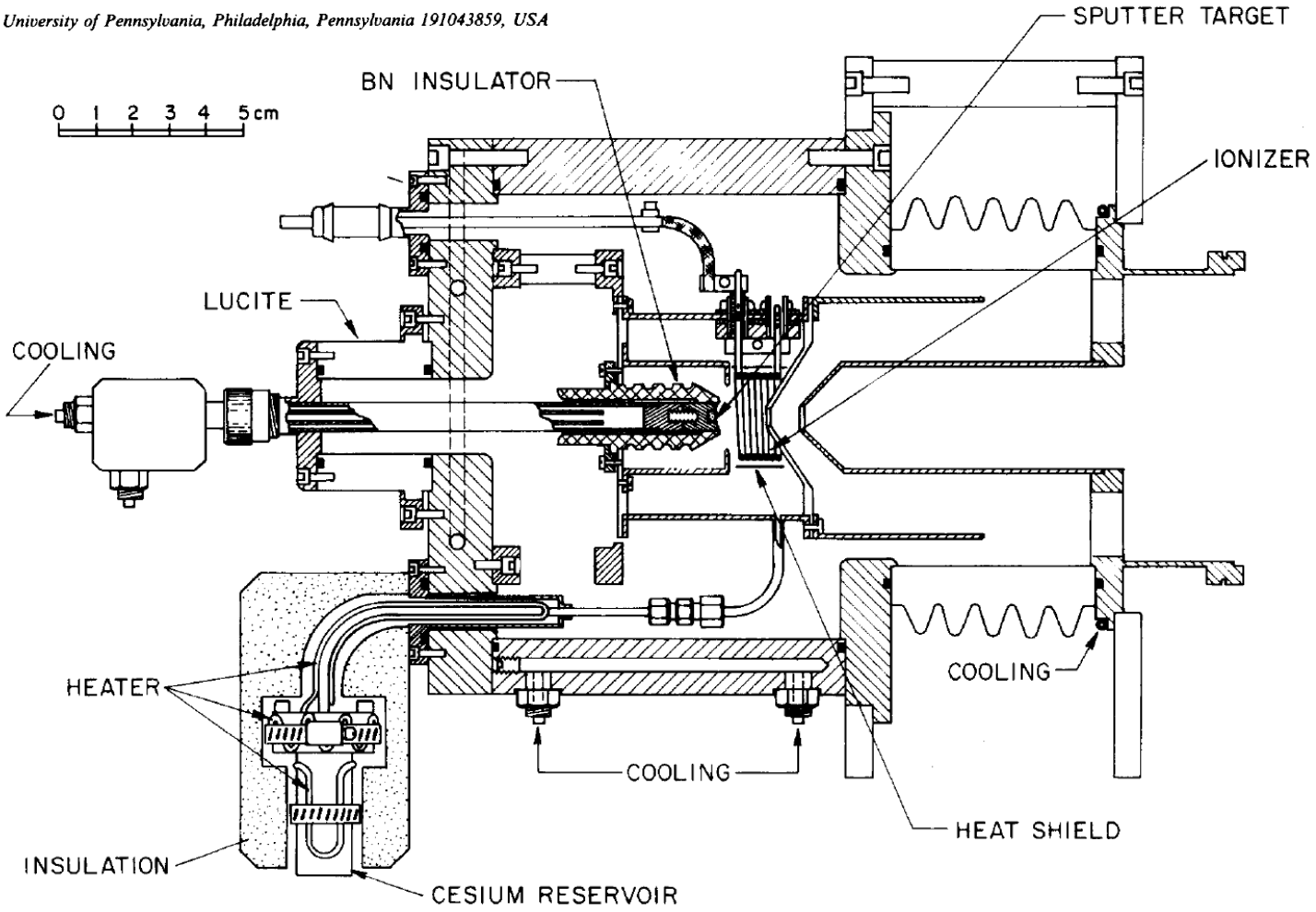
Nuclear Instruments and Methods in Physics Research 220 (1984) 105–106
North-Holland, Amsterdam

Cs sputtering negative ion source

Section III. Ion sources

A VERSATILE HIGH INTENSITY NEGATIVE ION SOURCE *

R. MIDDLETON
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 191043859, USA



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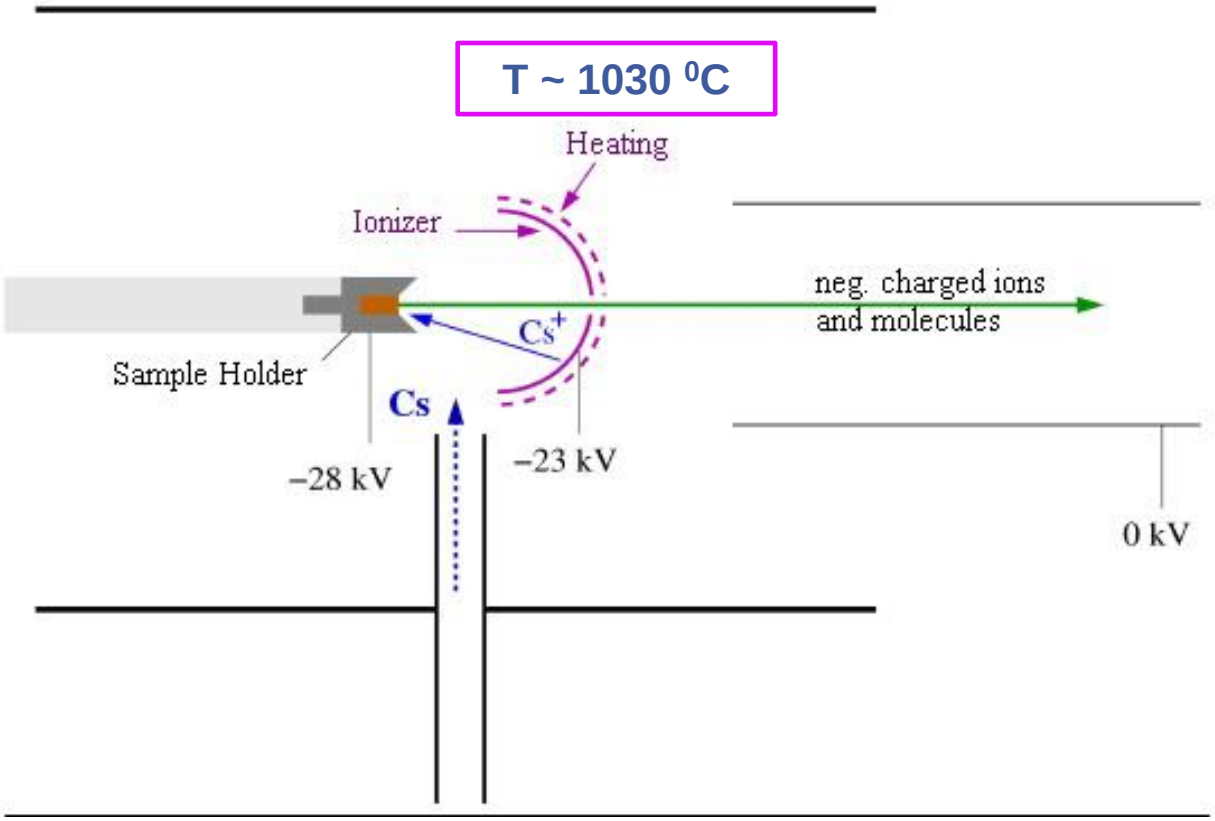
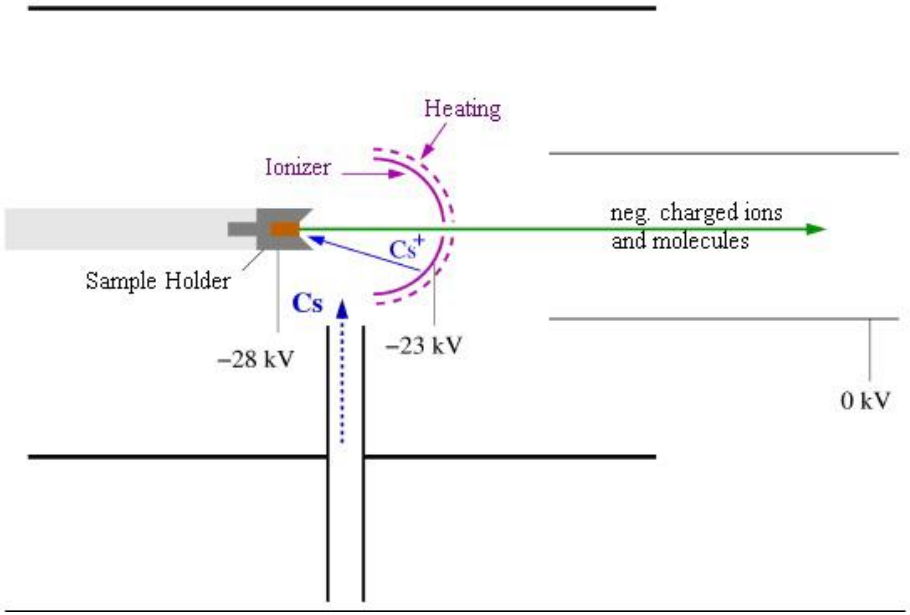


Diplomathesis P. Ludwig (2010) Schematic display of a high-current cesium sputter source of Middleton type with a spherical ionizer.

Cs sputtering negative ion source



~~$^{14}N^-$~~

~~$^{129}Xe^-$~~

$^{14}C^-$

$^{129}I^-$

$^{236}UO^-$

$^{244}PuO^-$

First possible atomic isobar separation

Diplomathesis P. Ludwig (2010) Schematic display of a high-current cesium sputter source of Middleton type with a spherical ionizer.

Sputtered AMS targets

Nuclear Instruments and Methods in Physics Research B 268 (2010) 820–823

Contents lists available at ScienceDirect

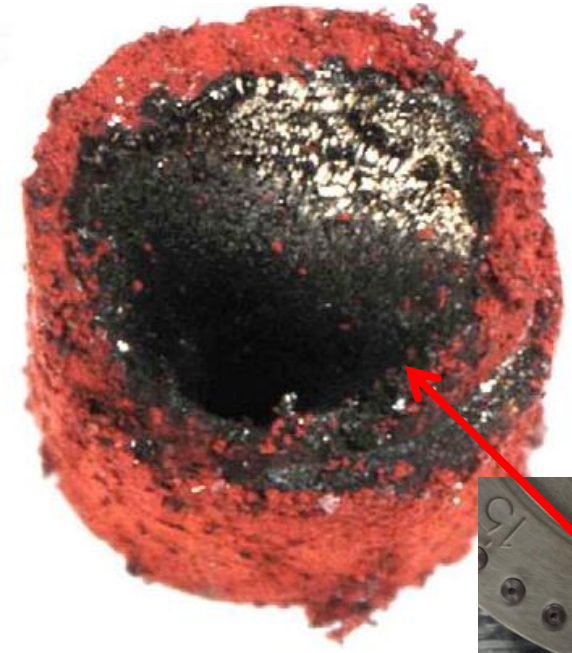
Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Ionisation efficiency improvements for AMS measurement of actinides

D.P. Child [a,*], M.A.C. Hotchkis [a], K. Whittle [a], B. Zorko [a,b]

[a] Australian Nuclear Science and Technology Organisation, PMB 1, Menai, NSW 2234 Australia
[b] Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

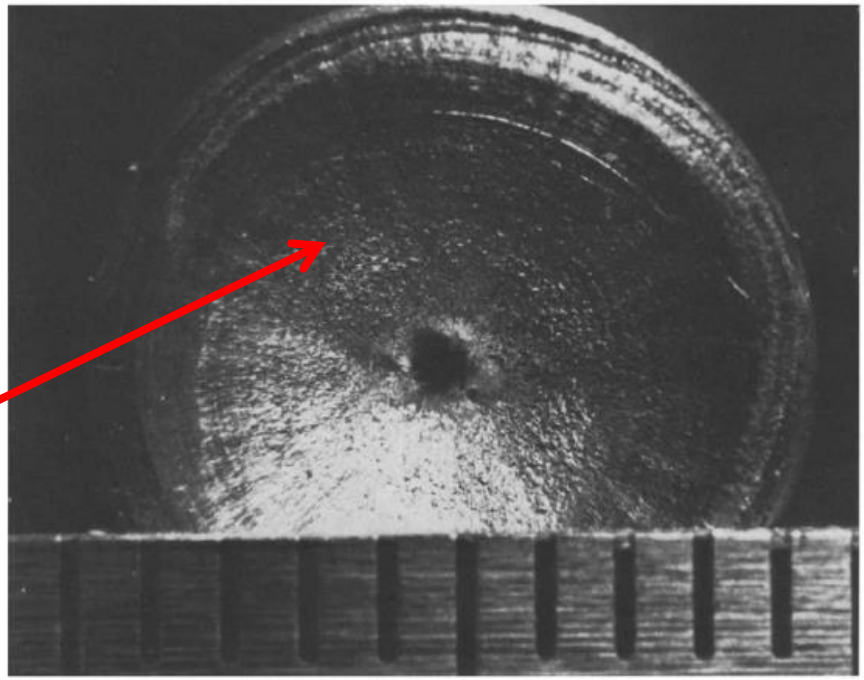


Nuclear Instruments and Methods 214 (1983) 139–150
North-Holland Publishing Company

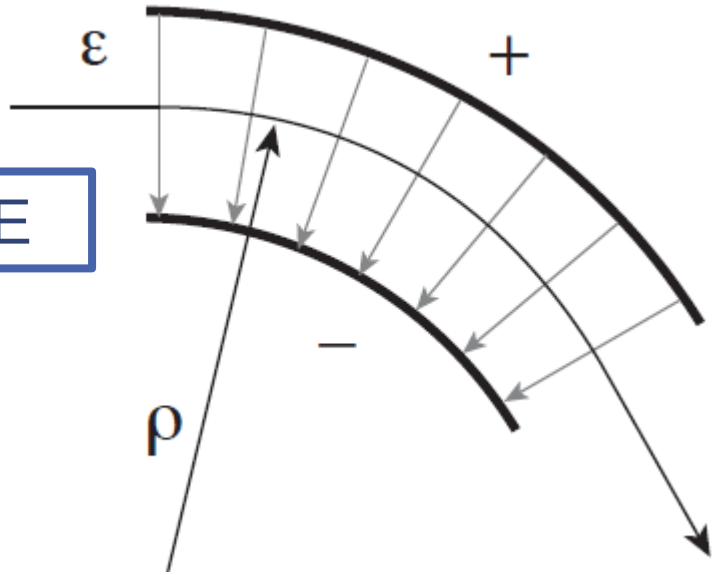
A VERSATILE HIGH INTENSITY NEGATIVE ION SOURCE *

R. MIDDLETON
Physics Department, University of Pennsylvania, Philadelphia, Pennsylvania 191043859, USA

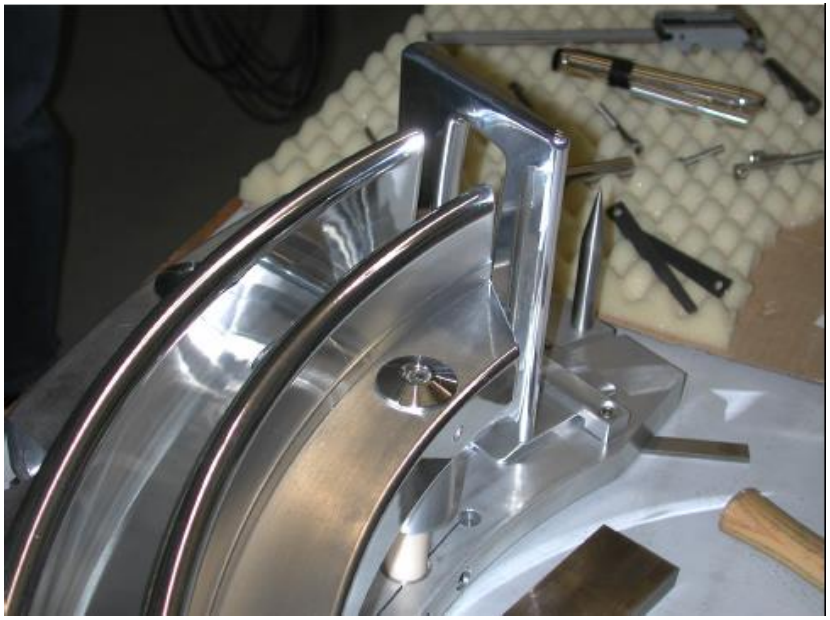
Received 23 December 1982



Electrostatic Analyzer - ESA



Selection of ions with a certain E

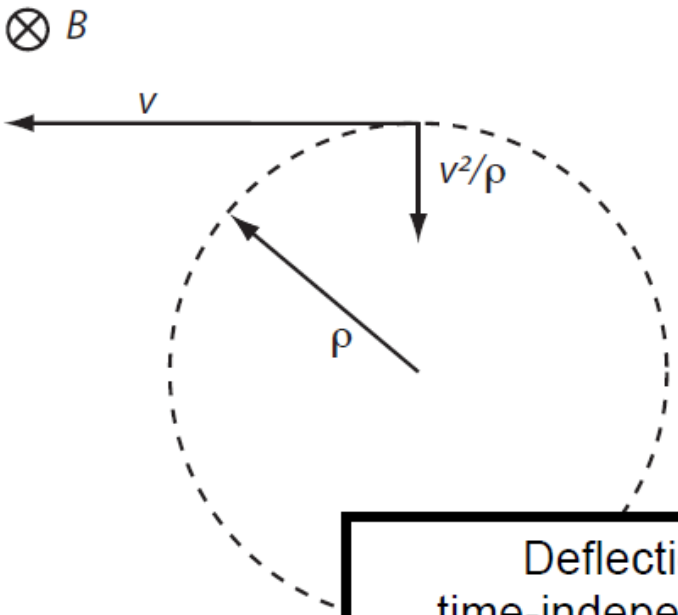


Deflection in a electric field between a pair of curved electrodes:

$$\varepsilon = \frac{\Delta U}{d}, \quad \varepsilon q = \frac{mv^2}{\rho}$$

$$\Rightarrow \varepsilon\rho = \frac{mv^2}{q} = \frac{2E}{q}$$

Dipole Magnet – 90^0



Selection of ions with a certain m/q

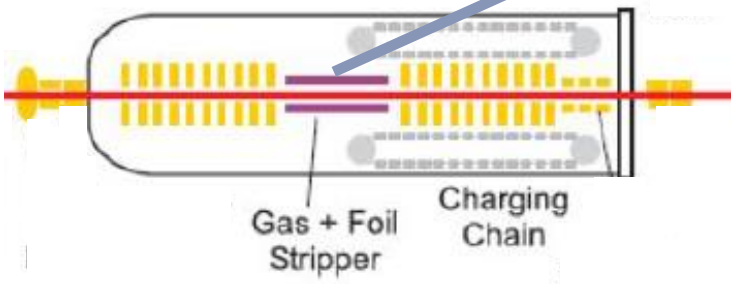
Deflection in a uniform, time-independet magnetic field:

$$Bqv = \frac{mv^2}{\rho}$$

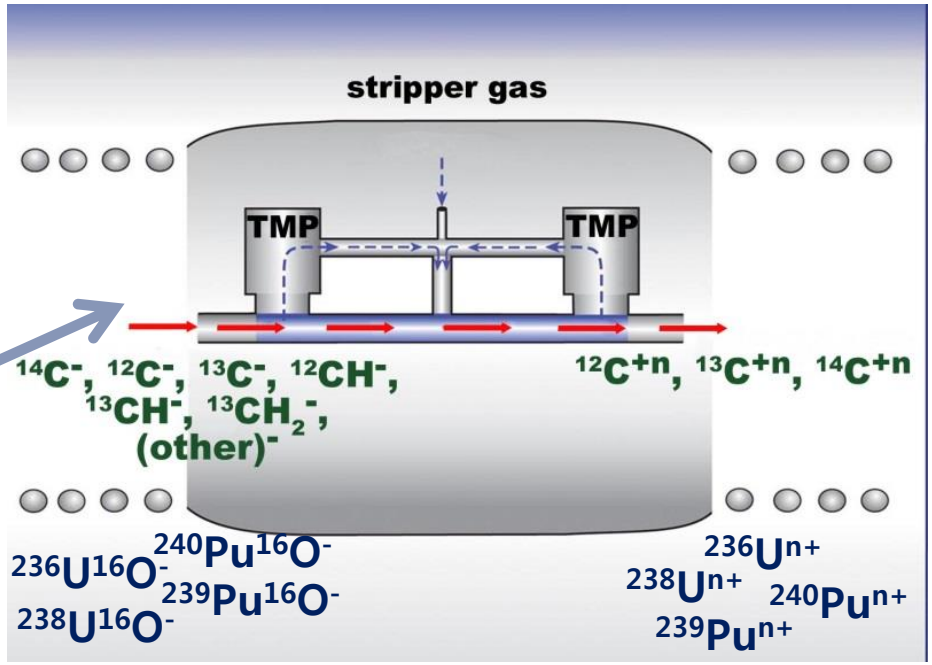
$$\Rightarrow B\rho = \frac{mv}{q} = \frac{p}{q} = \frac{\sqrt{2Em}}{q}$$

Background Suppression Device

Electrons Stripping =>
Molecular dissociation per
Coulomb explosion



Tandem Electrostatic Accelerator

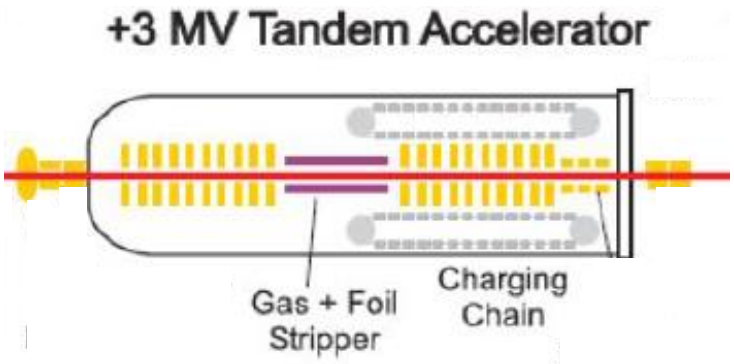


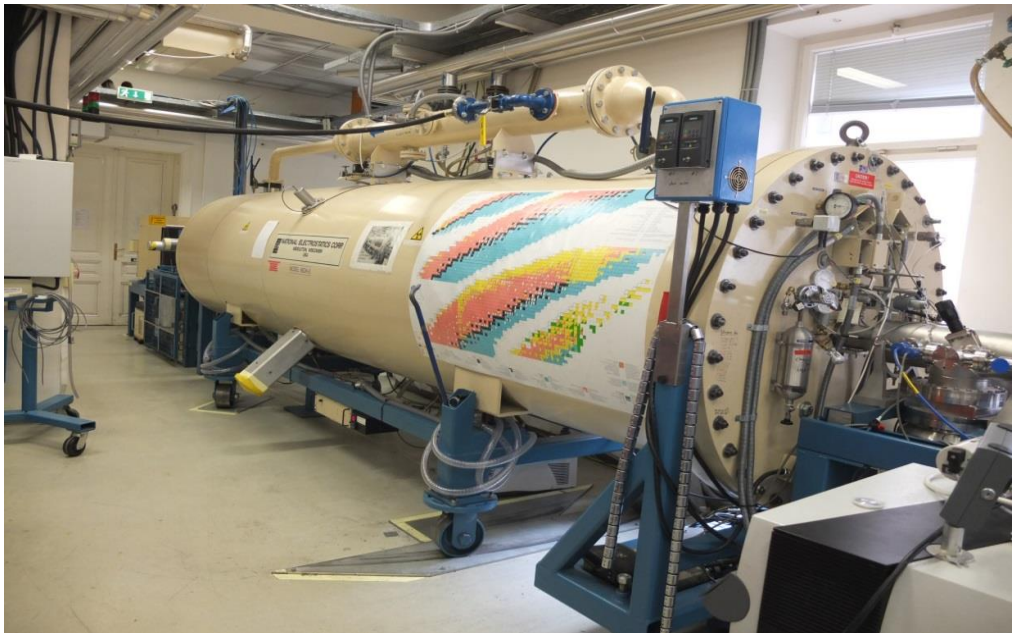
Destruction of molecular isobars

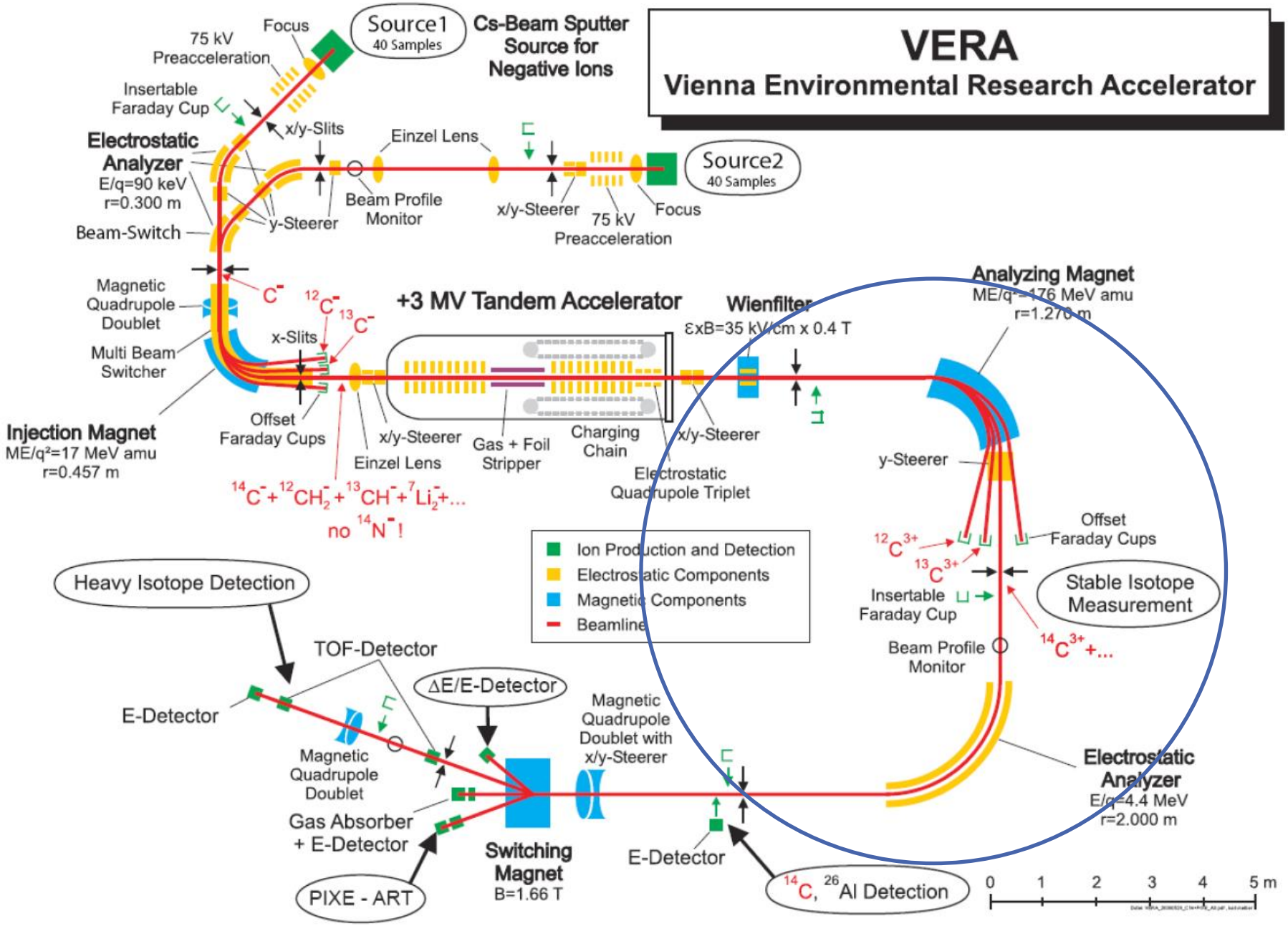
Tandem Electrostatic Accelerator

Kinetic energy of the monoatomic cations at the high energy end of the tandem - MeV

$$E = (E_{\mathrm{inj}} + \mathrm{e\,TV})\frac{M}{M_{\mathrm{inj}}} + q\,\mathrm{e\,TV}$$



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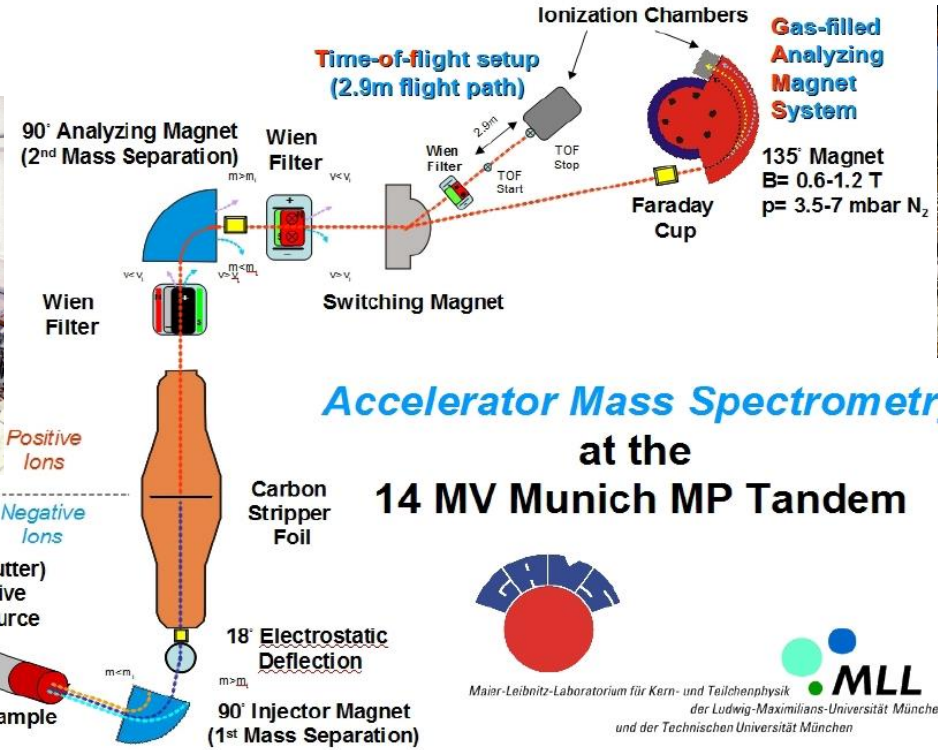
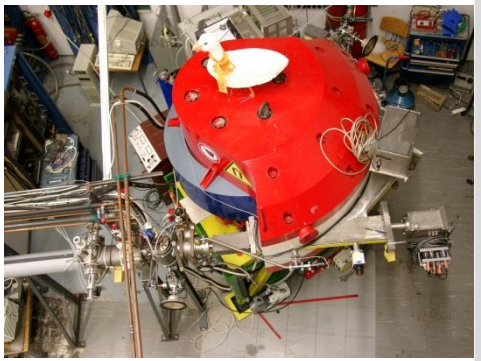
Gas-filled Analyzing Magnet System

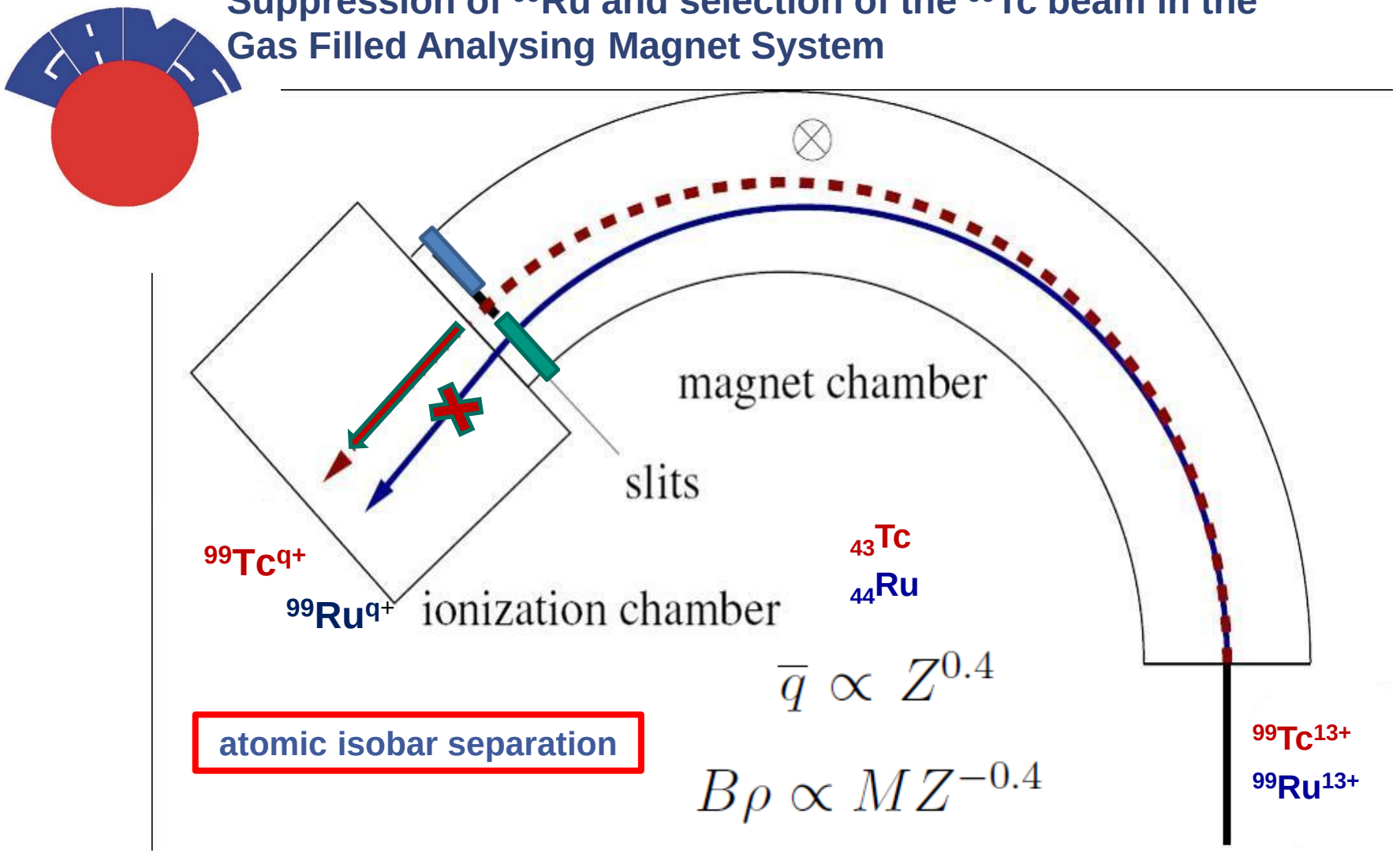
atomic isobar separation (e.g., ^{53}Mn – ^{53}Cr, ^{60}Fe - ^{60}Ni, ^{99}Tc – ^{99}Ru)





Background Suppression Device

Suppression of ^{99}Ru and selection of the ^{99}Tc beam in the Gas Filled Analysing Magnet System



atomic isobar separation

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International Journal of Mass Spectrometry 223–224 (2003) 713–732

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Karlsruhe Institute of Technology

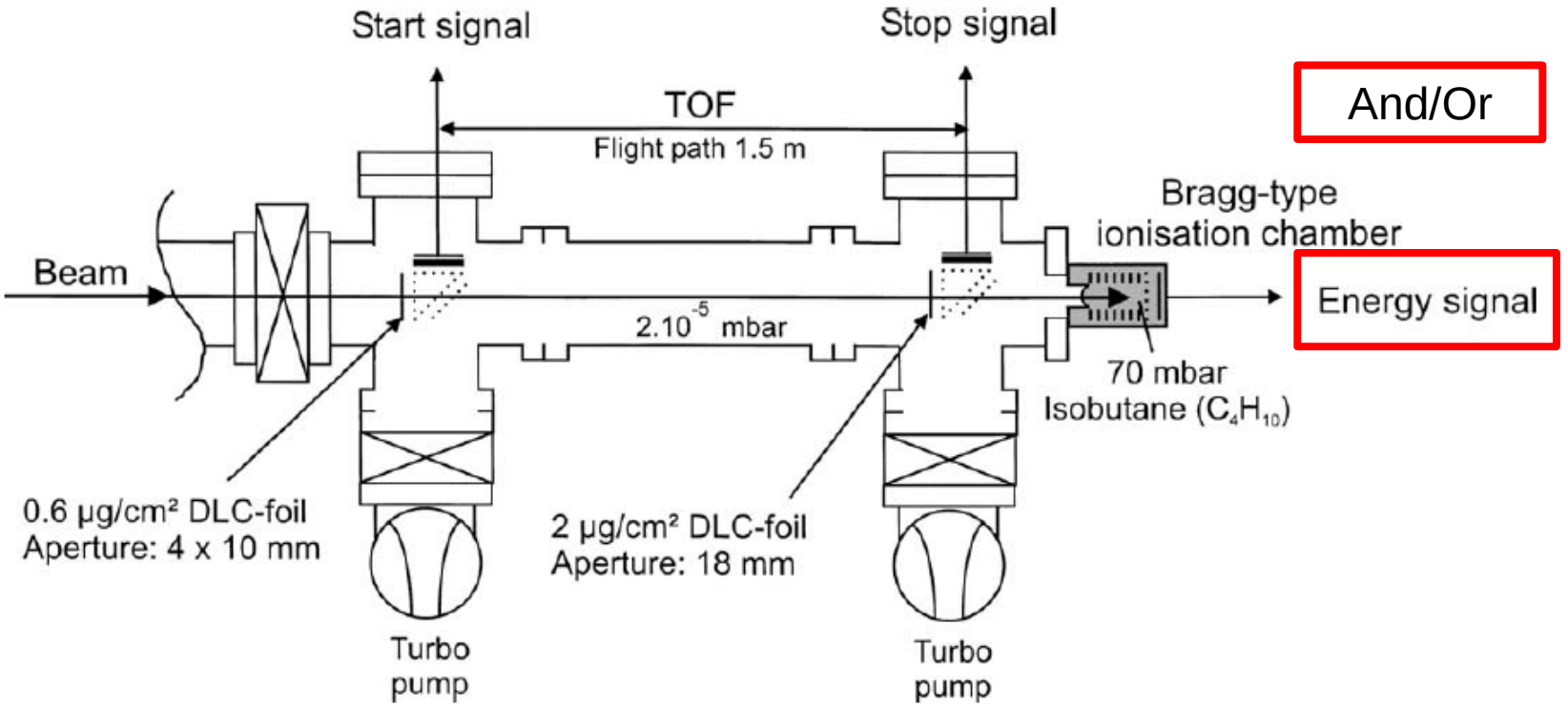
Ions Detection System

Accelerator mass spectrometry of heavy long-lived radionuclides

Christof Vockenhuber[a,*], Irshad Ahmad[b], Robin Golser[a], Walter Kutschera[a], Vitaly Liechtenstein[c], Alfred Priller[a], Peter Steier[a], Stephan Winkler[a]

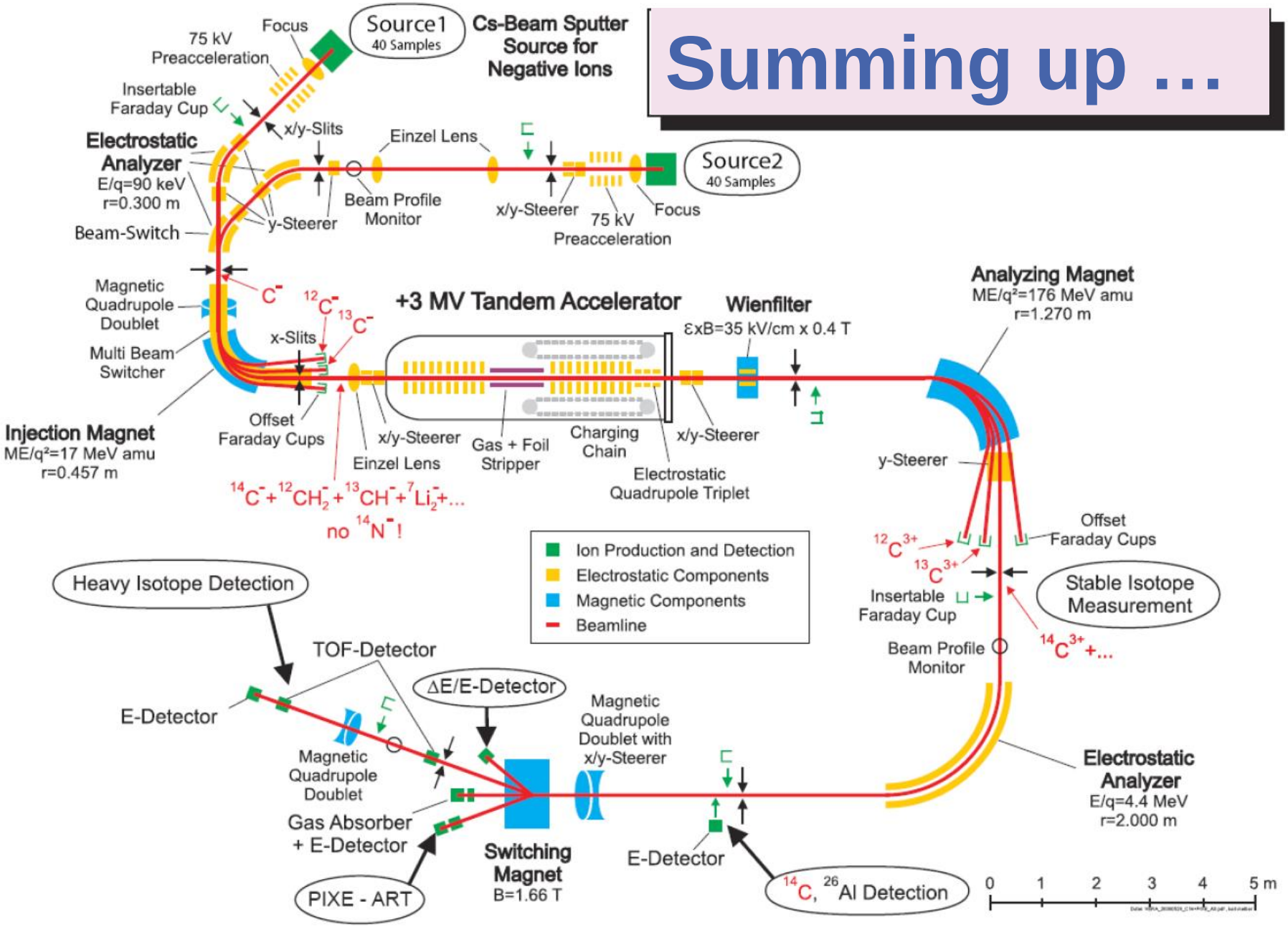
[a] *Vienna Environmental Research Accelerator, Institute for Isotopic Research and Nuclear Physics, University of Vienna, A-1090 Vienna, Austria*
[b] *Physics Division, Argonne National Laboratory, Argonne, IL 60439, USA*
[c] *Russian Research Center, "Kurchatov Institute", Institute of Nuclear Fusion, 123182 Moscow, Russia*

$$ToF = \frac{L \cdot m}{(B \cdot r) \cdot q}.$$



And/Or

Summing up …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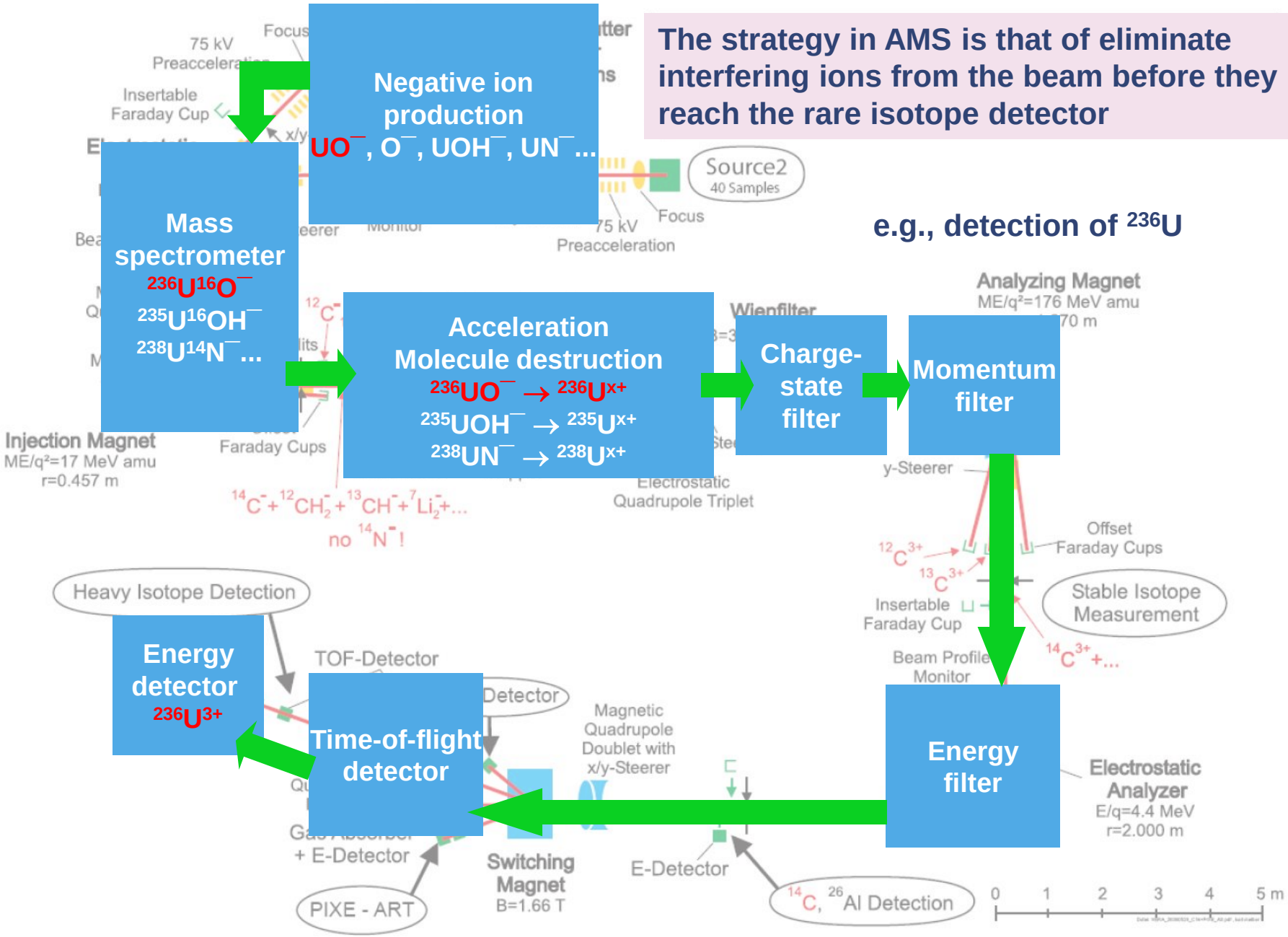
B=1.66 T
Magnetic Quadrupole Doublet with x/y-Steerer
E-Detector
14C, 26Al Detection
Electrostatic Analyzer
E/q=4.4 MeV
r=2.000 m
0 1 2 3 4 5 m

The strategy in AMS is that of eliminate interfering ions from the beam before they reach the rare isotope detector



Some of the RNs measured with the highest sensitivity with AMS

^{14}C ($t_{1/2}$ = 5700 ± 30 y)

In nature: spallation on ^{14}N target atoms in the atmosphere

$$^{14}\mathbf{N}\ (\mathbf{n}, \mathbf{p})\ ^{14}\mathbf{C}$$

In nuclear reactors and nuclear bomb tests:

$$^{14}\mathbf{N}\ (\mathbf{n}, \mathbf{p})\ ^{14}\mathbf{C}$$

$$^{13}\mathbf{C}\ (\mathbf{n}, \boldsymbol{\gamma})\ ^{14}\mathbf{C}$$

$$^{17}\mathbf{O}\ (\mathbf{n}, \boldsymbol{\alpha})\ ^{14}\mathbf{C}$$

Procedure Blanks $^{14}C/^{12}C$ ca. 10^{-15}
Range age for radiocarbon dating up to 50,000 y

In contemporary carbon $^{14}C/^{12}C = 1.2 \times 10^{-12}$

Several orders of magnitude higher

a wide range of $^{14}C/^{12}C$ ratios in environmental samples starting from 10^{-15}

AMS measurements of ^{14}C in seawater around radioactive waste dump sites

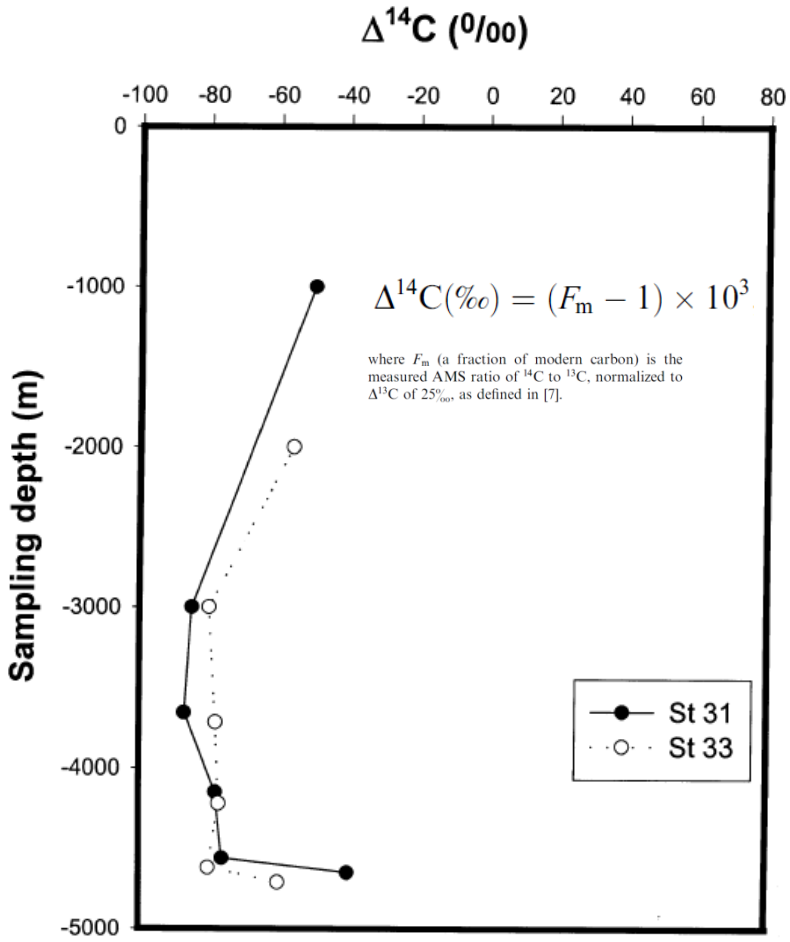


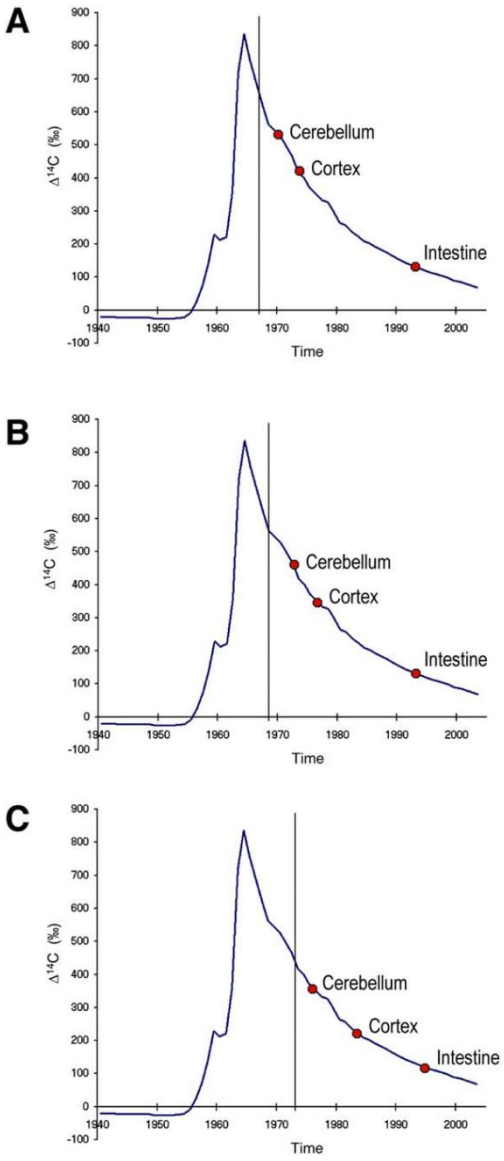
Fig. 2. ^{14}C water profiles in the NE Atlantic Ocean (1992).

Slightly elevated ^{14}C values observed close to the bottom interpreted as a continuous leakage of ^{14}C from dumped containers

Hypothesis supported by the observation of an elevated concentration of ^{238}Pu, $^{239,240}Pu$ and ^{241}Am with ratios higher than global fallout (not reported)

P.P. Povinec et al. / Nucl. Instr. and Meth. in Phys. Res. B 172 (2000) 672–678

Birth Dating of Cell in Humans with ^{14}C and AMS



Most molecules in a cell are in constant flux, with the unique exception of genomic DNA, which is not exchanged after a cell has gone through its last division

The level of ^{14}C integrated into genomic DNA should thus reflect the level in the atmosphere at any given point, and the authors hypothesized that determination of ^{14}C levels in genomic DNA could be used to retrospectively establish the birth date of cells in the human body

$$\Delta^{14}\mathrm{C}(‰) = (F_{\mathrm{m}} - 1) \times 10^3$$

Cell, Vol. 122, 133–143, July 15, 2005, Copyright ©2005 by Elsevier Inc. DOI 10.1016/j.cell.2005.04.028

Some of the RNs measured with the highest sensitivity with AMS

^{129}I ($t_{1/2}$ = 15.7 ± 0.4 My)

In nature:
spallation on Xe target atoms in the atmosphere and
spontaneous fission of ^{238}U

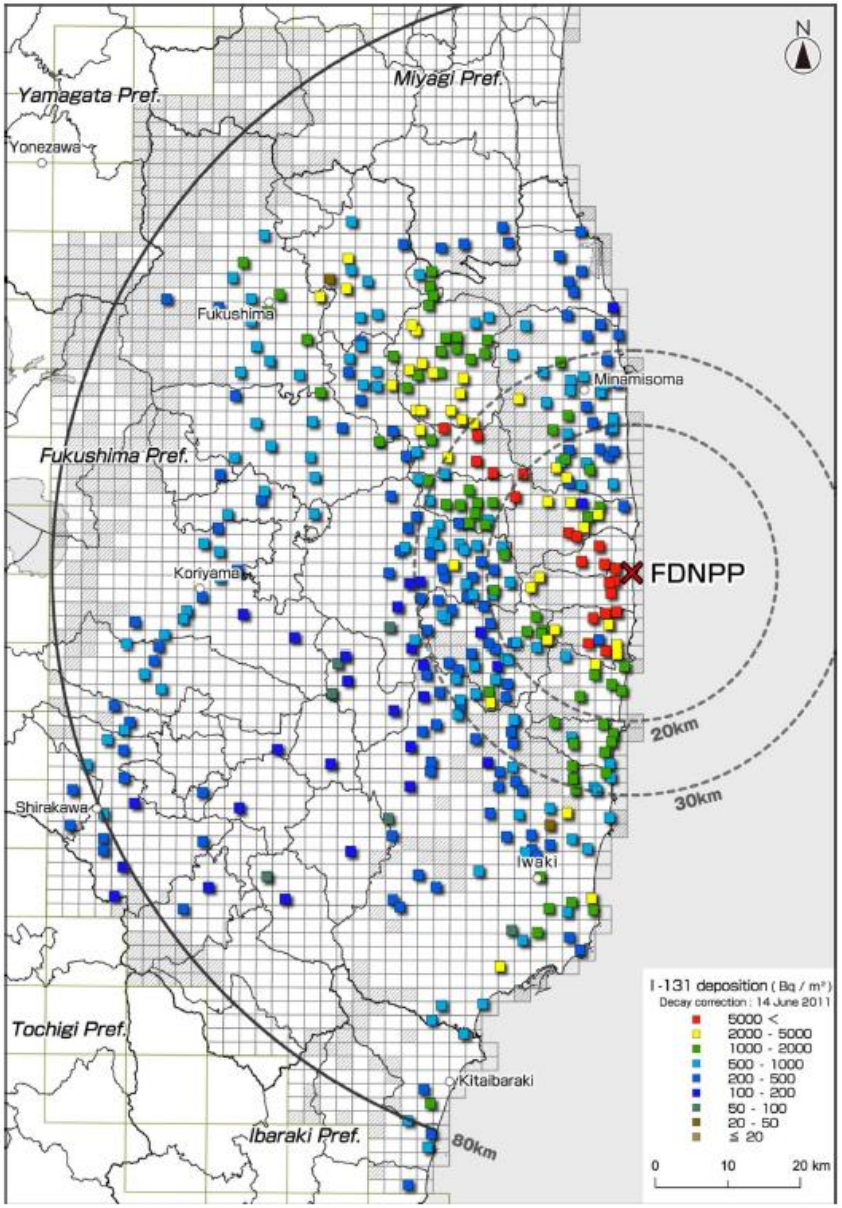
In nuclear reactors and nuclear bomb tests:
fission of ^{235}U and ^{239}Pu

a wide range of $^{129}I/^{127}I$ ratios in environmental samples spanning from below 10^{-14} to up to 10^{-6}

Retrospective dosimetry of ^{131}I after nuclear accidents by measuring ^{129}I with AMS

Following the accident, the short half life of ^{131}I (8 d) made it impossible to obtain adequate sample coverage for a direct determination of the regional deposition patterns

Small amounts of ^{129}I produced in the reactor were also released during the accident with a ratio $^{129}I/^{131}I$ almost constant in the samples were both RNs could have been measured



Deposition map (Bq/m^2) of ^{131}I reconstructed from ^{129}I analysis in Fukushima Prefecture.

Y. Muramatsu et al. / Journal of Environmental Radioactivity 139 (2015) 344–350

Some of the RNs measured with the highest sensitivity with AMS

^{236}U ($t_{1/2}$ = 23.42 My)

In nature:
spontaneous neutron capture on ^{235}U

$$^{235}U\ (n,\gamma)\ ^{236}U$$

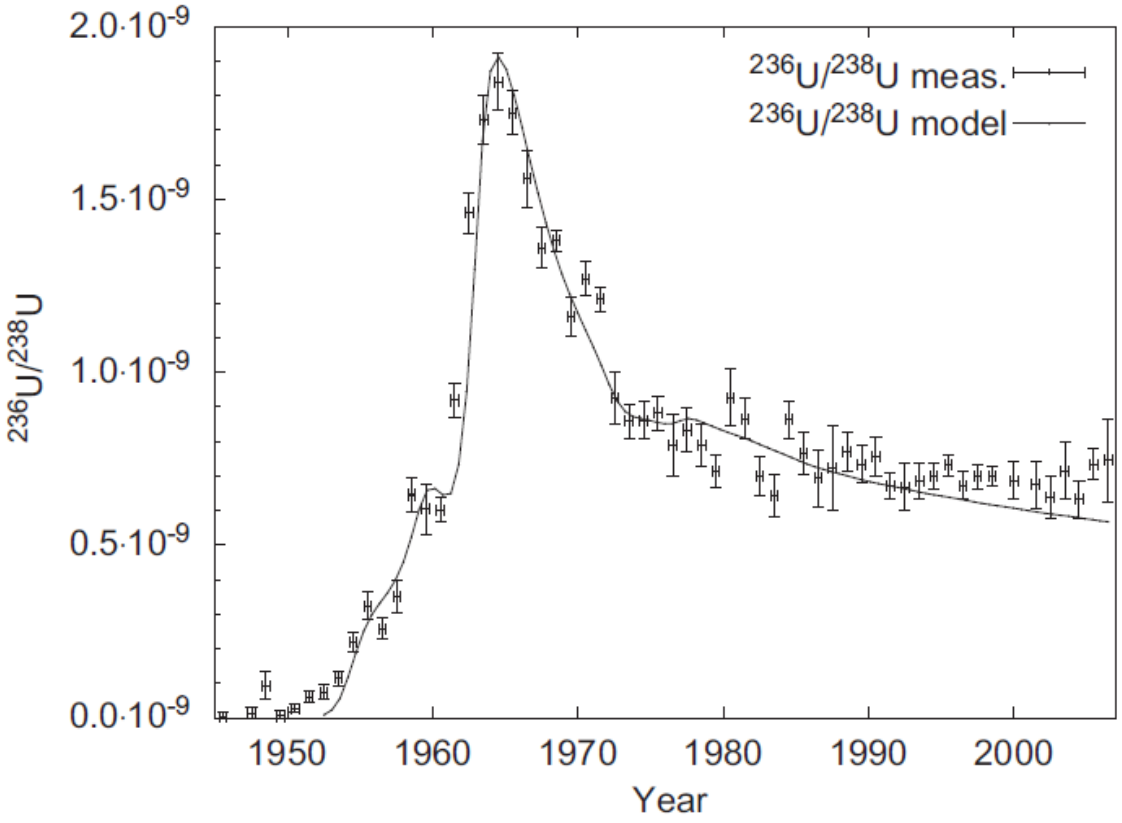
In nuclear reactors and nuclear bomb tests:

$$^{235}U\ (n,\gamma)\ ^{236}U$$

$$^{238}U\ (n,3n)\ ^{236}U$$

a wide range of $^{236}U/^{238}U$ ratios in environmental samples spanning from below 10^{-14} to up to 10^{-2}

^{236}U as oceanic tracer: The investigation of reliable geological archives in the form of coral cores



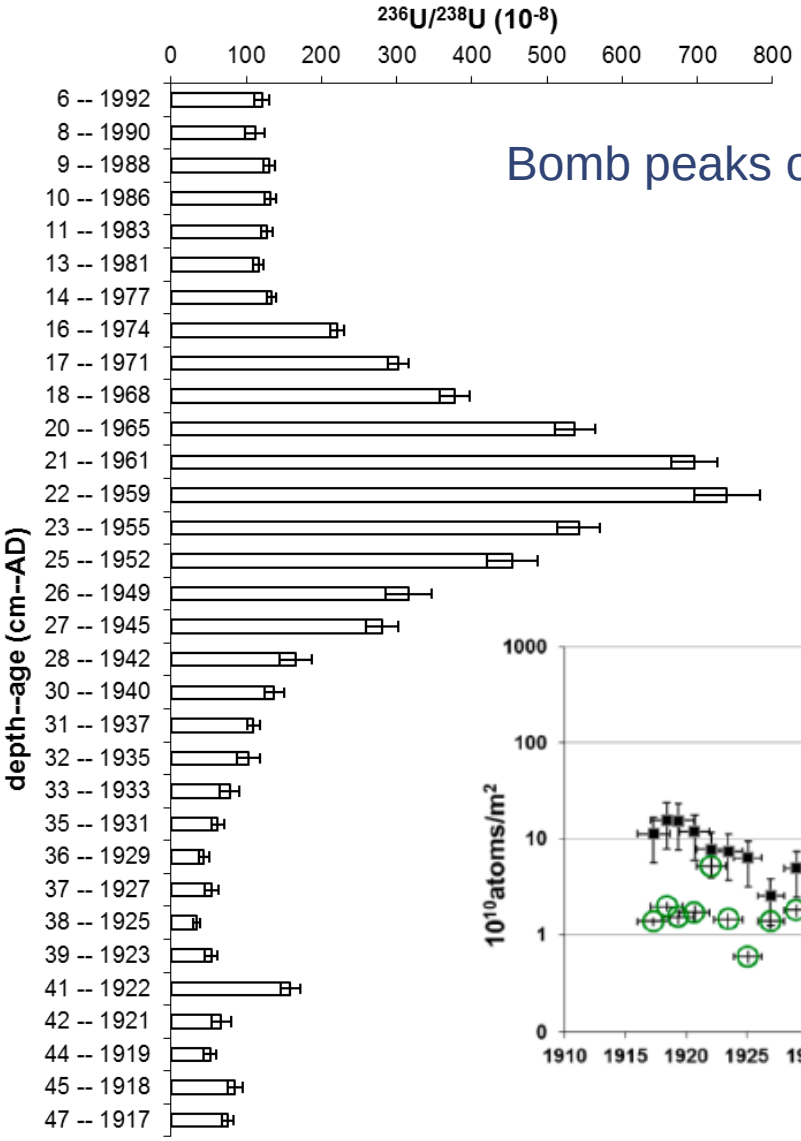
Corals build uranium into their aragonite skeleton at a level of 2-4 ppm by substitution of uranium for calcium in the lattice

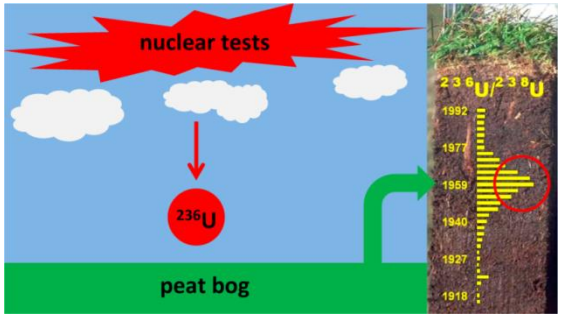
An ideal archive to trace the input of ^{236}U by nuclear testing and further evolution in the ocean

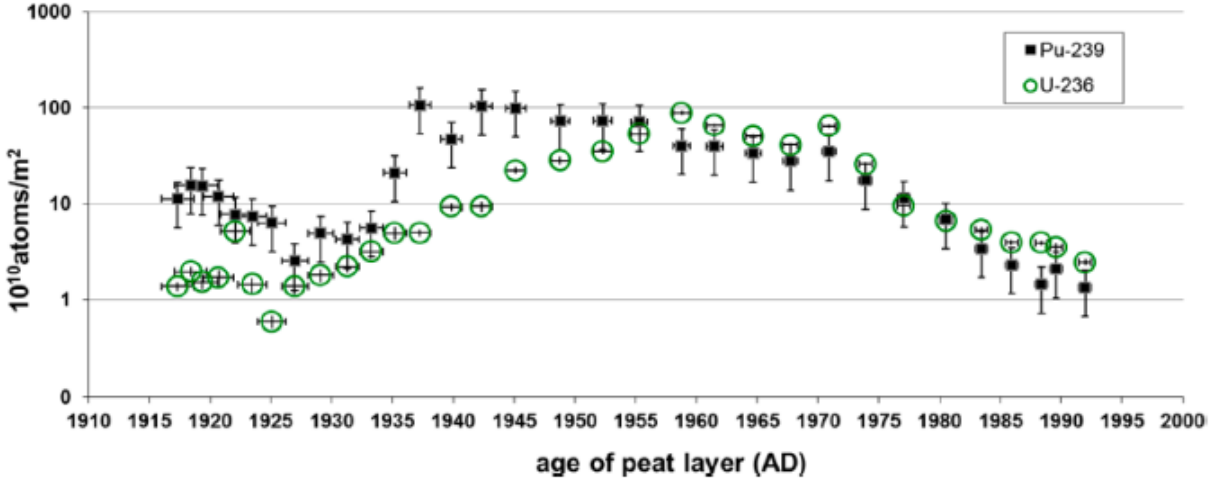
Bomb pulse of ^{236}U in an annually resolved coral core from the Caribbean Sea

S.R. Winkler et al. / Earth and Planetary Science Letters 359-360 (2012) 124–130

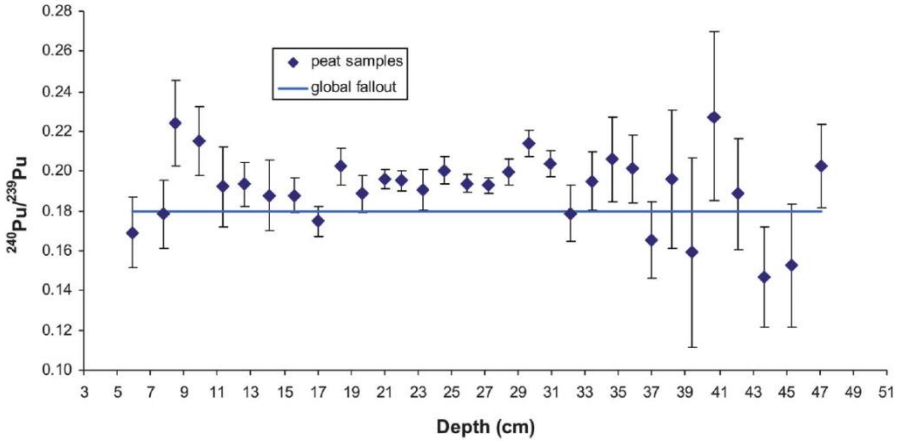
Bomb peaks of ^{236}U and ^{239}Pu along the ^{210}Pb dated profile of an ombrothrophic peat bog core



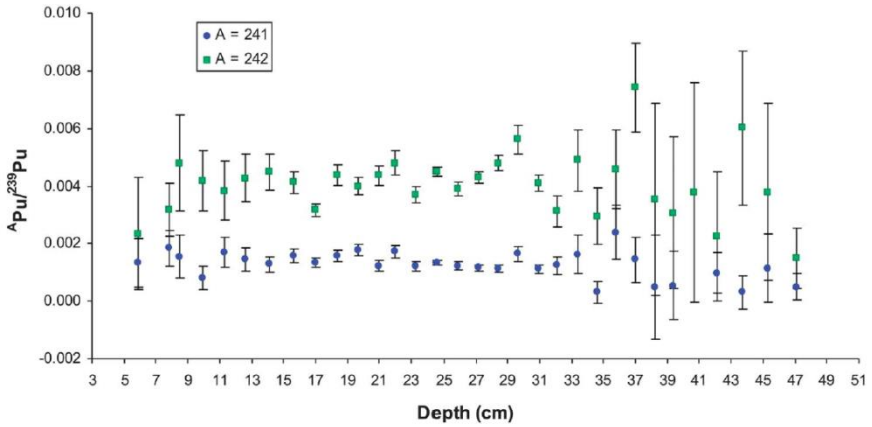


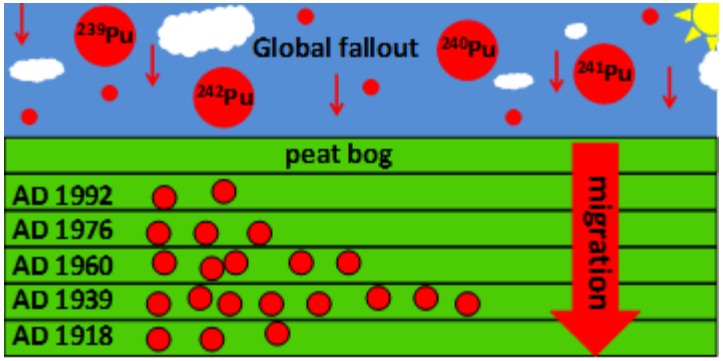


dx.doi.org/10.1021/es400026m | *Environ. Sci. Technol.* 2013, 47, 5243−5250



Isotopic ratios of $^{2340,241,242}Pu/^{239}Pu$ along the profile of the ombrotrophic peat bog core revealing the oring of plutonium from stratospheric nuclear weapon tests



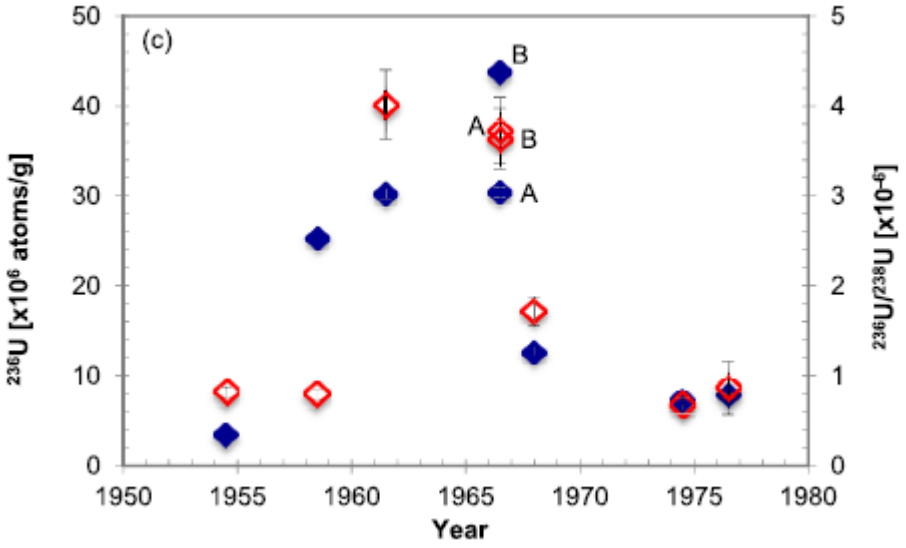


Environ. Sci.: Processes Impacts, 2013, **15**, 839–847

Bomb peak of ^{236}U in roe deer antlers

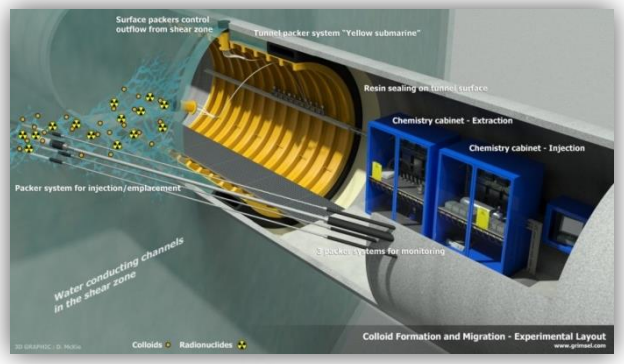
roe deer shed their antlers annually, and hence antlers may provide a time-resolved environmental archive for fallout radionuclides

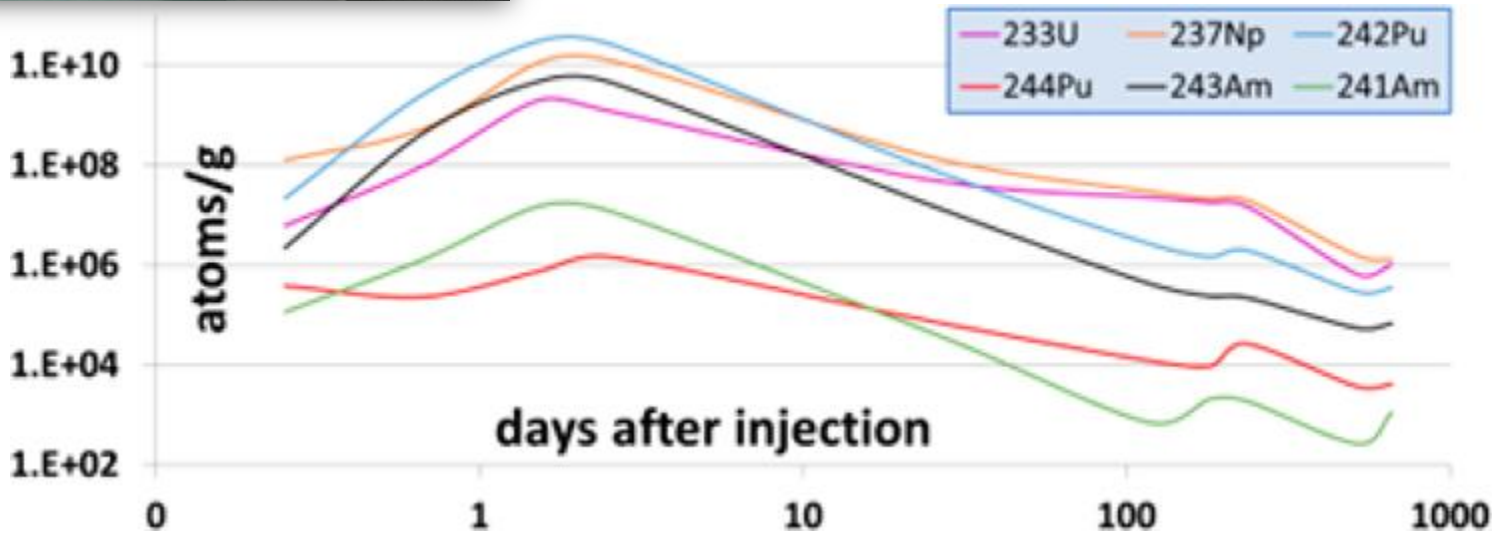
The antlers were hunting trophies, and hence the hunting area, the year of shooting and the approximate age of each animal was known



Journal of Environmental Radioactivity 151 (2016) 587–592

Safety of geological nuclear waste disposal – in situ radionuclide tracer tests at the Grimsel Test Site





DOI: 10.1021/acs.analchem.7b01359
Anal. Chem. 2017, 89, 7182−7189

Summing up

The strategy in AMS is that of eliminate interfering ions from the beam before they reach the rare isotope detector

AMS the most sensitive analytical technique for the investigation of rare long-lived radionuclides in the environment

at least 4 and up to 7 orders of magnitude less atoms than a radiometric technique to perform equally precise measurements, with consequent reduction of sample size

unambiguous nuclide detection in environmental samples at concentration levels below ppq

Fields of Application:

Archeology
Biomedical research
Environmental science
Geology
Monitoring of nuclear contamination
Nuclear Physics and Astrophysics
Safety of nuclear waste disposal

Karlsruhe Institute of Technology

Thank you for your kind attention!