Application of the Pyrolyser for analysis of environmental samples, including determination of I-129

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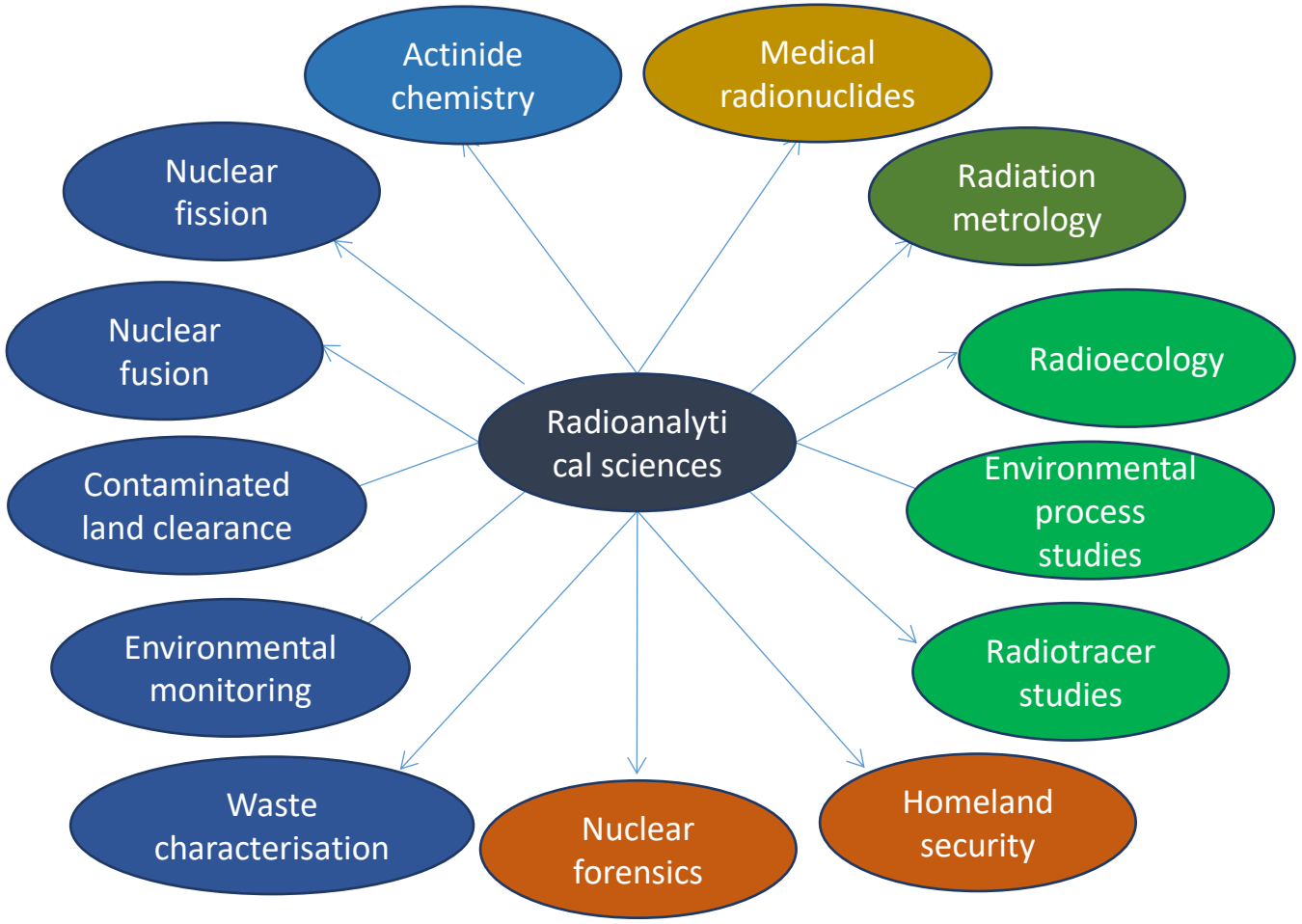
Main application fields of radioanalytical Chemistry

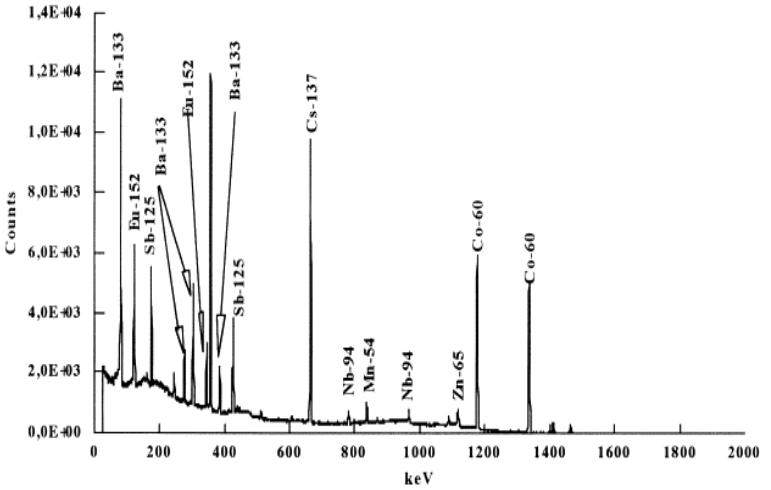


- Origination of nuclear materials by isotope ratios, dispersion and transfer of radionuclides
- Level, distribution, variation and migration of radionuclides in environment, radiological risk
- Production of nuclear fuel, spent fuel reprocessing, repository and migration of radionuclides
- Monitoring of influencts, characterization of radioactive waste from nuclear facilities and decommissioning
- Quality control of medical radionuclides, biological metablism of radiopharceutics, radiation impact
- Dating of geological events with radionuclides. Tracing dispersion of air, water and contaminants

Major Radionuclides in the environment and nuclear waste

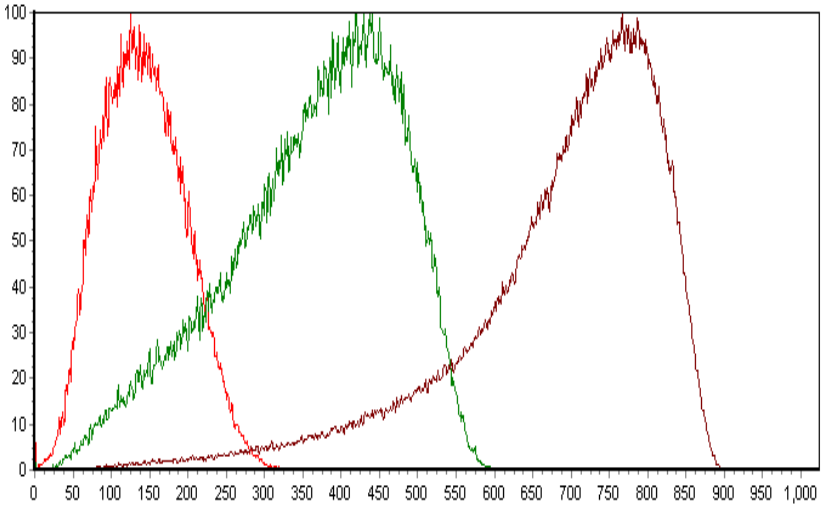
- γ- radionuclides

  ^{60}Co, ^{133}Ba, ^{137}Cs, ^{134}Cs, ^{106}Ru, $^{152,154,155}Eu$, ^{58}Co, ^{54}Mn, ^{59}Fe, ^{110m}Ag, ^{94}Nb.



Difficult-to-measure radionuclides

- β- Emitter
  - ^{3}H, ^{14}C, ^{36}Cl, ^{99}Tc, ^{129}I, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{93}Zr, ^{93}Mo, ^{90}Sr, ^{241}Pu
- α- emitter (actinides)
  - $^{238\text{-}240}Pu$, ^{241}Am, $^{243,244}Cm$, ^{237}Np



Radioanalysis of Radionuclides

Sampling

Pre-concentration

γ- spectrometry
(**^{137}Cs, ^{134}Cs,** ^{131}I, ^{241}Am)

Radiochemcial separation of target radionuclides from matrix and interferring radionuclideds

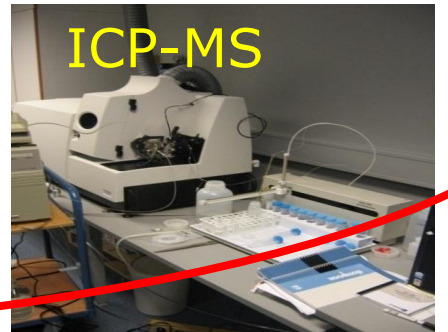
β- couting
(^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, **^{99}Tc, ^{90}Sr**)

α- spectrometry
(^{238,239,240}Pu,^{241}Am,^{242}Cm, ^{210}Po, ^{226}Ra, ^{222}Rn)

AMS
(**^{129}I, ^{236}U, ^{14}C, ^{36}Cl, ^{59}Ni, ^{41}Ca**)

ICP-MS
(^{135}Cs, ^{239}Pu, ^{240}Pu, ^{237}Np, **^{99}Tc**)

Other MS



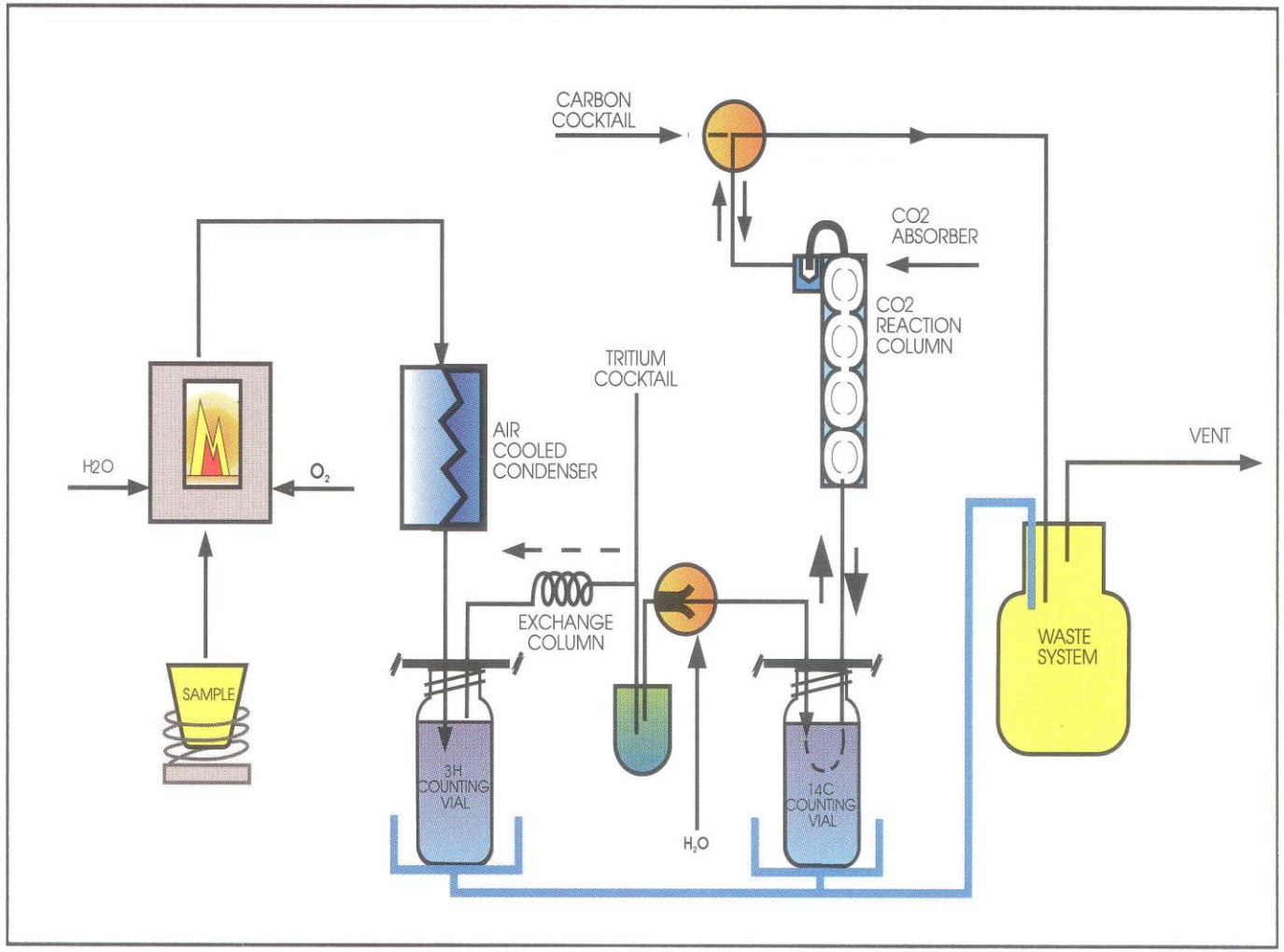
Radiochemcial analysis of volatile radionuclides

- ^{3}H and ^{14}C in solid waste (soil, filter/particles, biotas, metals, concrete, graphite, etc.)
- ^{36}Cl in solid samples（metals, graphite, concrete, etc.）
- ^{99}Tc in solid samples (soil, sediment, biotas, resin, slug, etc)
- ^{129}I in solid samples (soil, sediment, vegetation, animal tissues, exchange resin, evaporate, etc.)
- $^{103, 106}Ru$, ^{210}Po, etc.

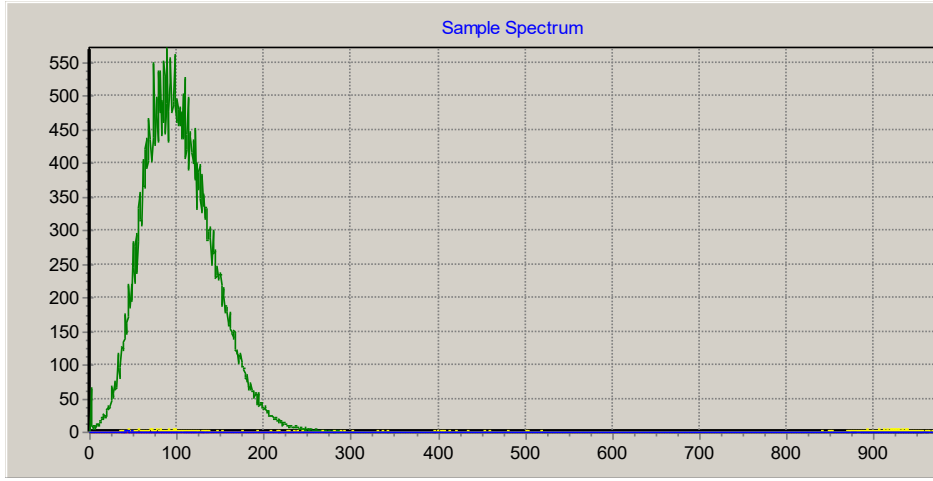
Main challenge: loss of radionuclides during sampling, pre-tratement and separation.

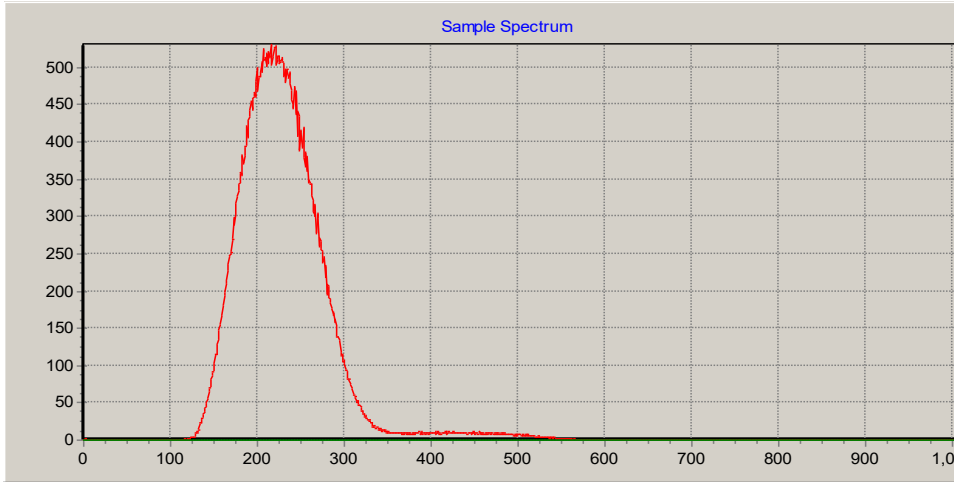
Strategy: Application of combustion for their separation

Rapid separation of ^{3}H and ^{14}C waste samples by combustion using Packard Oxidizer



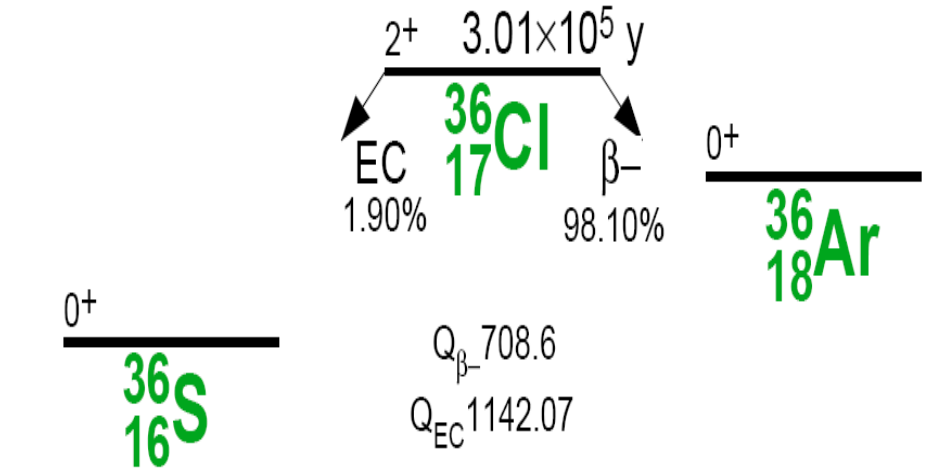
Hou., Appl. Rad. Iso., 2005
Hou, JRNC, 2008

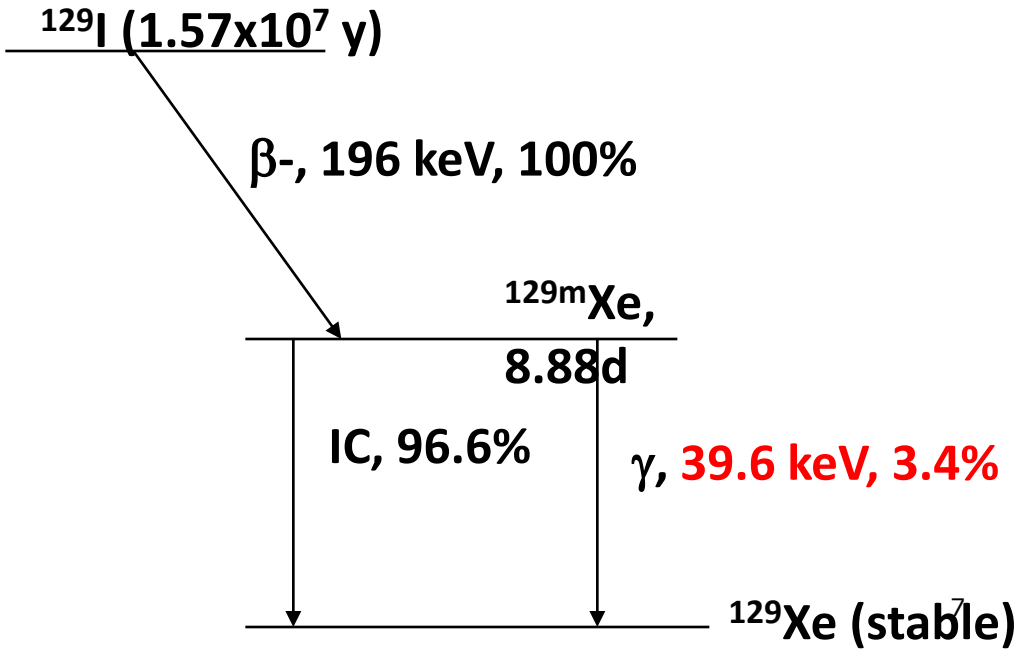




- **Analytical time: 2 min/sample**
- **Detection limits:**
  - **^{14}C: 0.1 Bq**
  - **^{3}H: 0.15 Bq**

^{36}Cl and ^{129}I

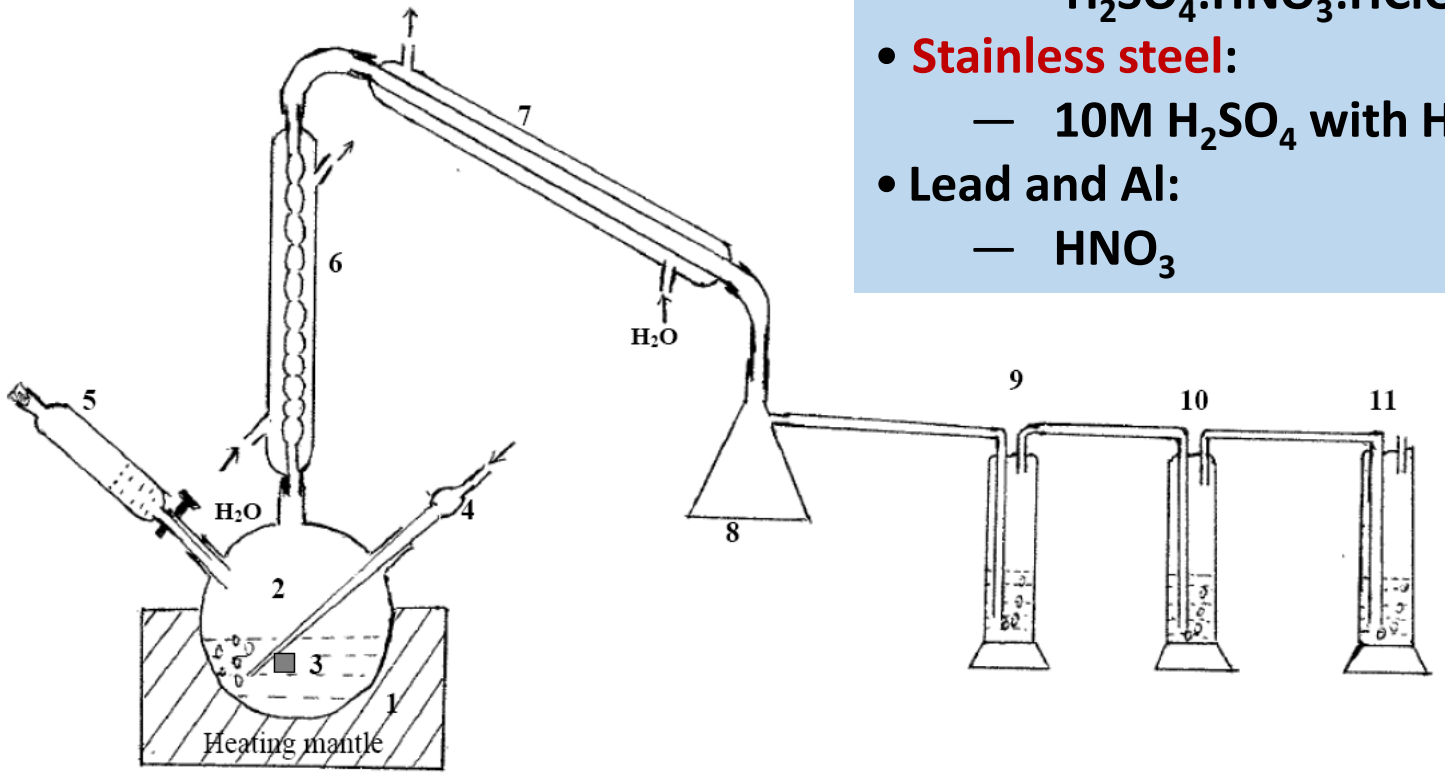




- **Iodine and chlorine are volatile, easy to be lost during heating or by oxidizing.**
- **^{36}Cl and ^{129}I are long-lived radionuclides (0.3 My, and 15.7 My)**
- **Iodine and chlorine are high mobile in environment.**
- **Iodine and chlorine are biophilic.**

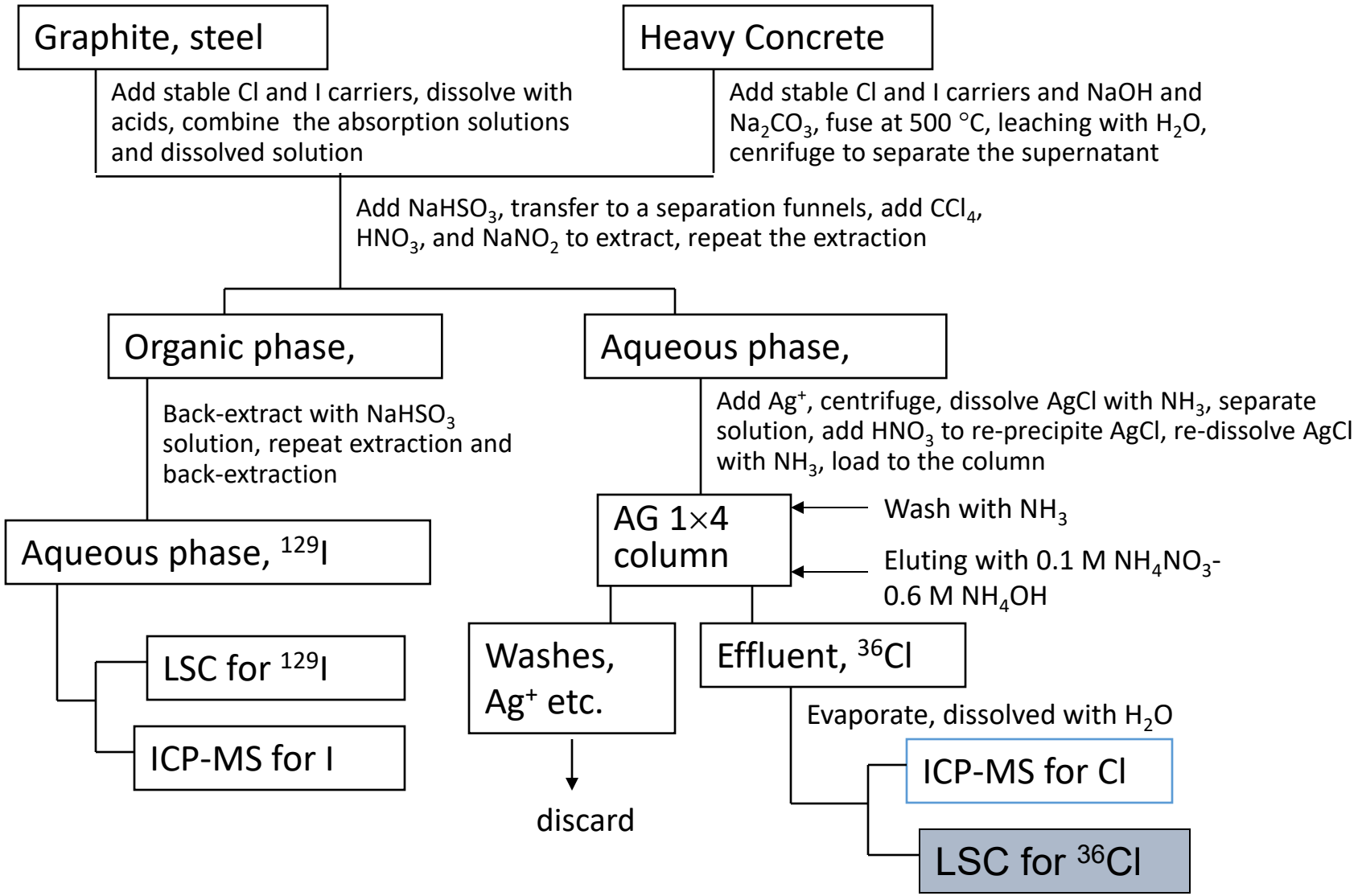
Acid digestion system of for separation of ^{36}Cl and ^{129}I

- **Graphite**: mixed acids,
  - — H_2SO_4:HNO_3:$HClO_4$ =15:4:1
- **Stainless steel**:
  - — 10M H_2SO_4 with H_3PO_4
- **Lead and Al**:
  - — HNO_3



1-Heating mantle; 2-three-necked flask; 3-sample in acid mixture; 4-bubbling tube; 5-separating funnel for adding acids; 6,7-reflux condenser; 8- receiver; 9-wash bottle containing water; 10, 11-absorption bottles containing 0.4 mol/l NaOH

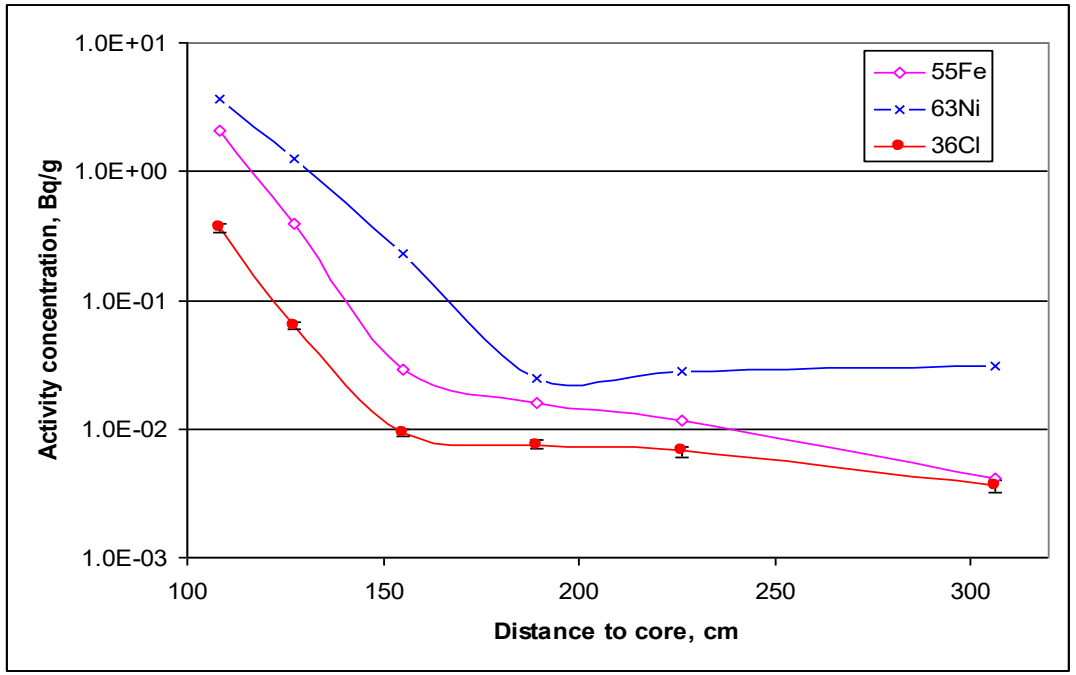
Analytical procedure for ^{36}Cl and ^{129}I



Hou et al., Anal. Chem., 2007

Determination of ^{36}Cl

- Recovery of Cl: >70%
- Decontamination factors for most of radionculides: $>10^6$
- Detection limit using LSC : 14 mBq

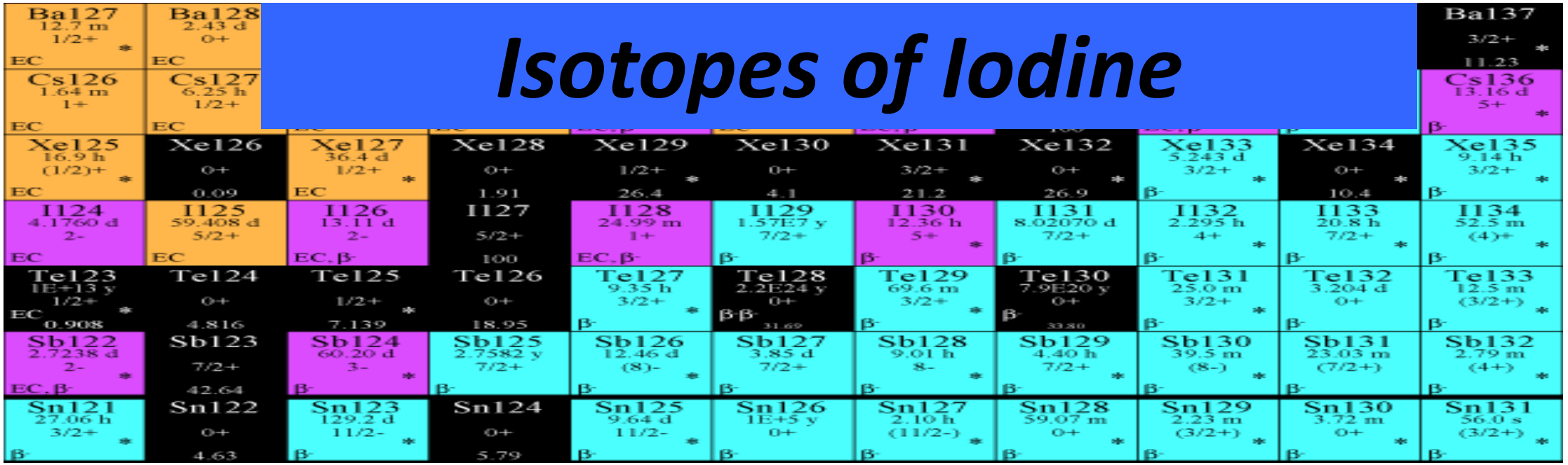


Combustion method for solid samples: concrete, graphite, metals, resin, sludge, etc.

- ✓ ^{3}H
- ✓ ^{14}C
- ✓ ^{129}I
- ✓ ^{36}Cl
- ✓ ^{99}Tc

Hou et al., Anal. Chem., 2010
Hou, et al. JAAS, 2016

Isotopes of Iodine



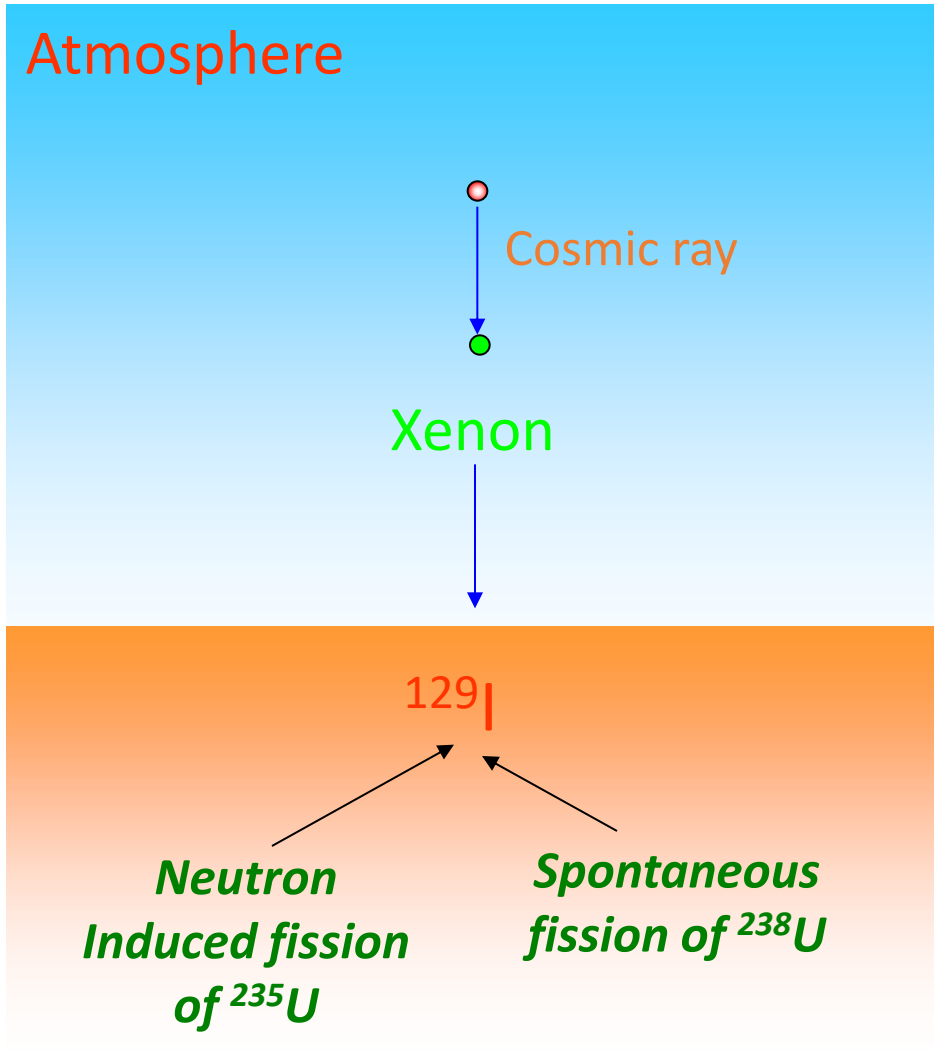
- ^{127}I (stable, 100% abundance)
- ^{131}I (8 d),
- ^{125}I (56 d),
- ^{126}I (13 d), ^{124}I (4.2 d)
- ^{129}I (15.7×10^6 years)
- others (< 1 day)

Properties of iodine

- Chemically active element with oxidation state of -1, 0, +1, +3, +4, +5, +7, e.g. I^-, I_2, IO^-, IO_3^-, IO_4^-
- The most popular species of iodine in the environment are: I^-, IO_3^- and organic iodine.
- **Iodine is considered as a n volatile element, based on the volatile feature of the species of I_2, CH_3I, etc.**
- Iodine is considered as a conservative element on the ocean, because it mainly presents as iodate, and iodide in some waters.

Source of ^{129}I

- **Natural process:**



- **Artificial process:**

$^{235}U(n, f)\ ^{129}I$

$^{239}Pu(n, f)^{129}I$

^{129}I level in environment

Source	Release/ inventory, kg	$^{129}I/^{127}I$ ratio
Nature	250	10^{-12}
Nuclear weapons testing	63	10^{-10}~10^{-9}
Chernobyl accident	1.3~6	10^{-9}~10^{-6} (local)
Marine discharge of EU NRPs	5200	10^{-7}~10^{-6} (seawater)
Atmospheric emission from NRPs	800	10^{-6}~10^{-4} (local)

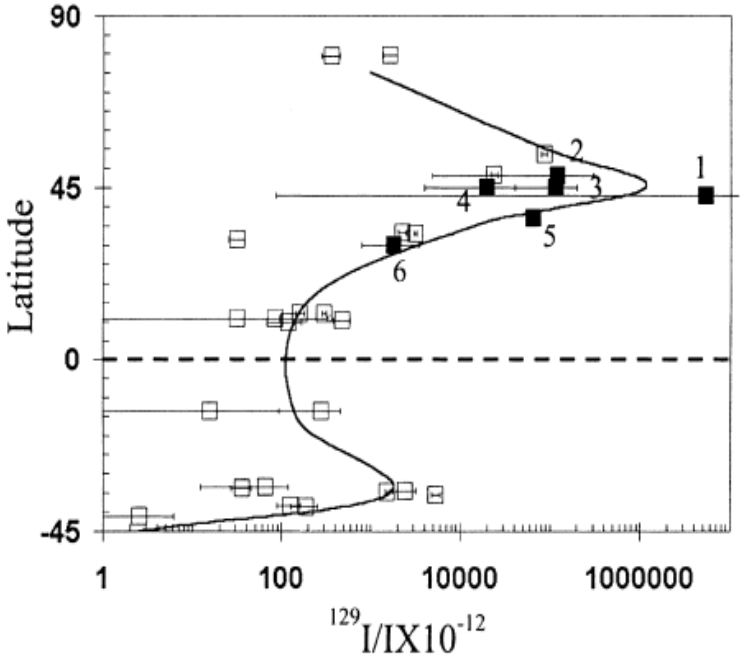
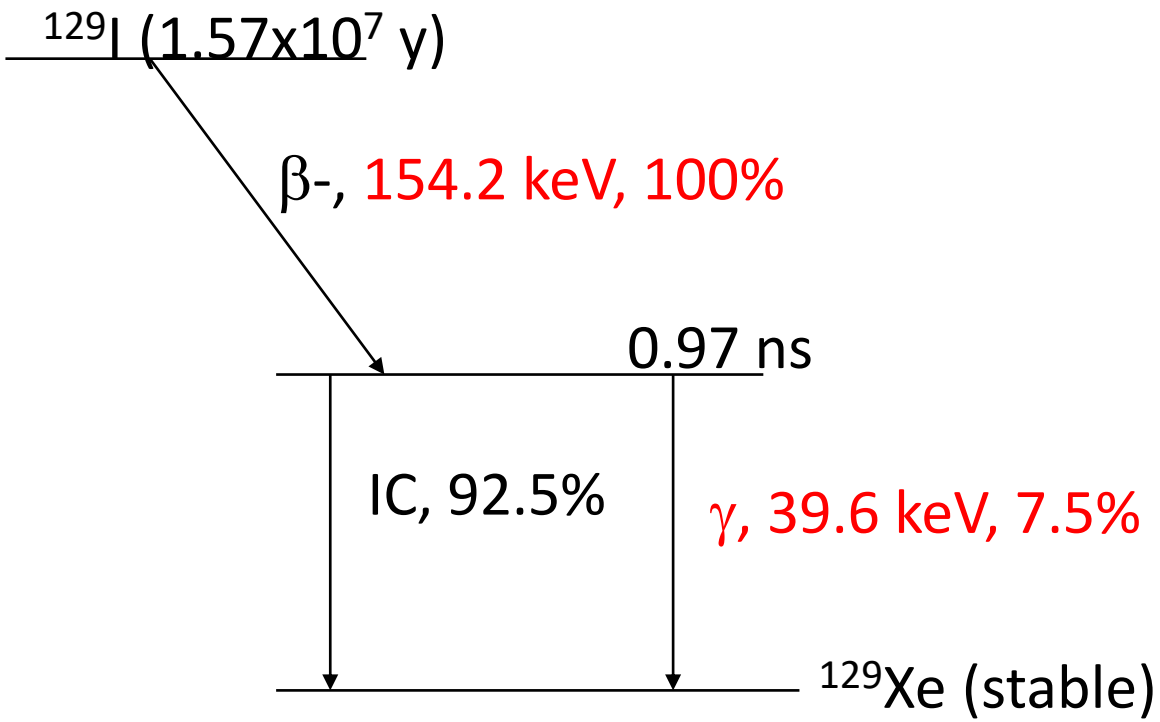


Fig. 1. $^{129}I/I$ ratios in surface waters as a function of latitude. Open squares indicate samples with associated errors (1 σ)

Decay of ^{129}I and its radiation



X-rays:
29.5 keV, 20.4%
29.8 keV, 37.7%
33.6 keV:10.1%

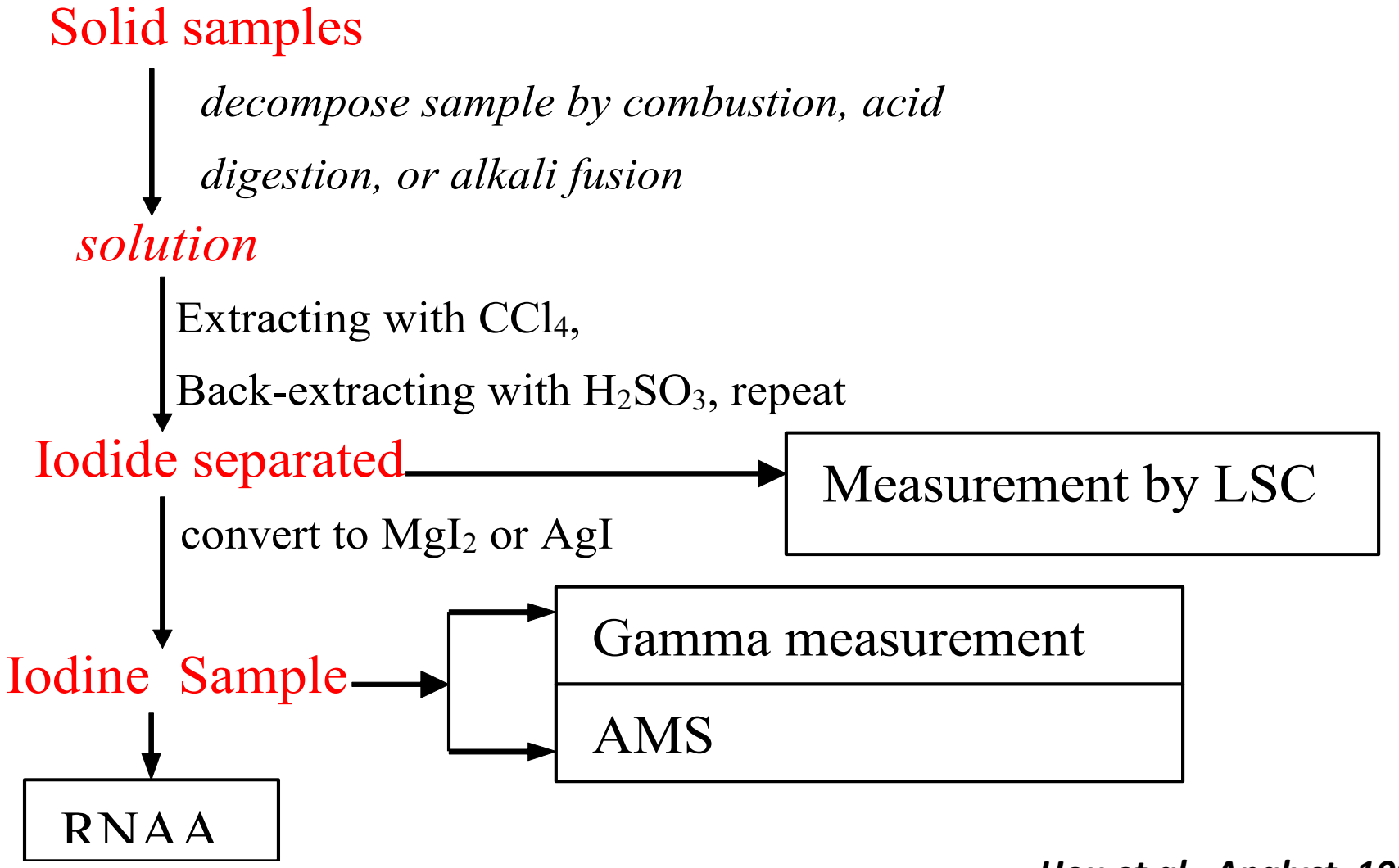
Measurement Method for ^{129}I and their detection limits

Method	Detection limit		
	^{129}I, atoms	^{129}I, mBq	**$^{129}I/^{127}I$ Ratio**
Liquid scintillation	**10^{13}**	10 mBq	
γ-spectrometry	**10^{13}**	10 mBq	
ICP-MS	**2×10^{11}**	0.4 mBq	**10^{-6}**
Radiochemical neutron activation analysis	**10^{8}**	**0.2 mBq**	**10^{-10}**
Accelerator mass spectrometry (AMS)	**10^{5}**	**0.1 nBq**	**10^{-13}**

Hou et al. ACA, 2007

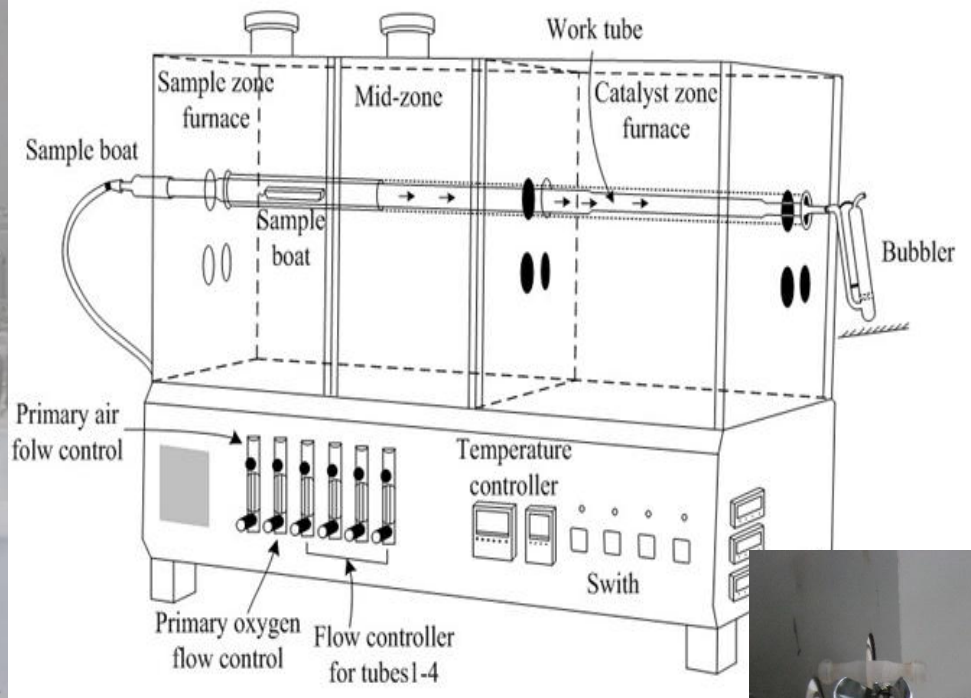
Separation procedure of iodine from solid samples

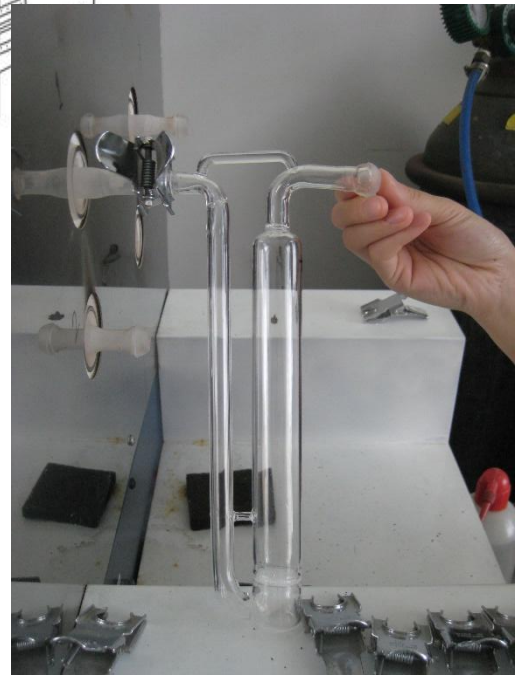
(seaweed, soil, sediment, filter, vegetation, etc.)



Hou et al. Analyst, 1999

Separation of iodine from solid samples using Pyrolyser





- The working tube bubbler and joint are quartz materials to avoid the reaction of I_2 with plastic material
- Combustion is controled by the gas composition and flow rate
- No catalyst materials

Separation of iodine from soil/sediemnt using combustion

Parameters influencing the separation of iodine by combustion:

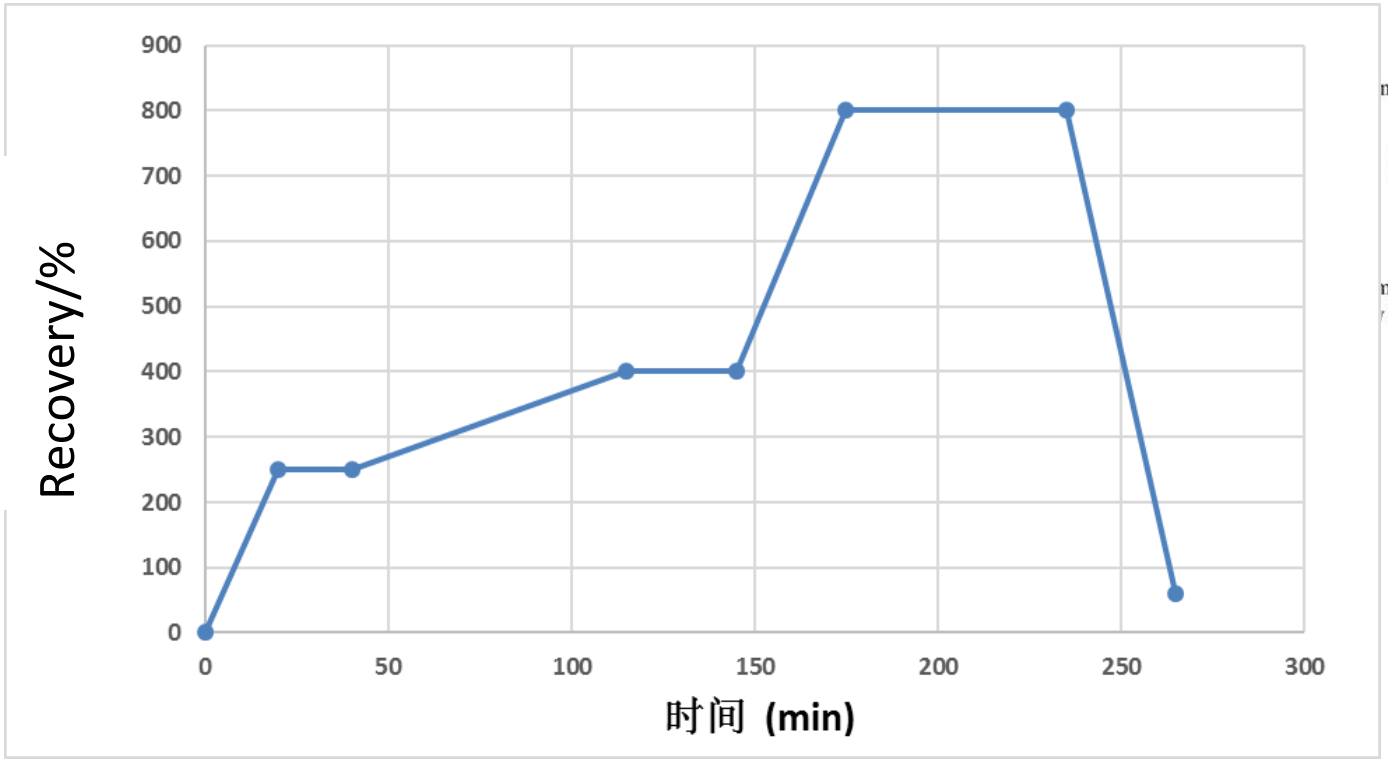
- **Trap solution and the concentrations**
- **combustion protocol and temperature**
- **Combustion time time**
- **Carrier gases and flow rate**

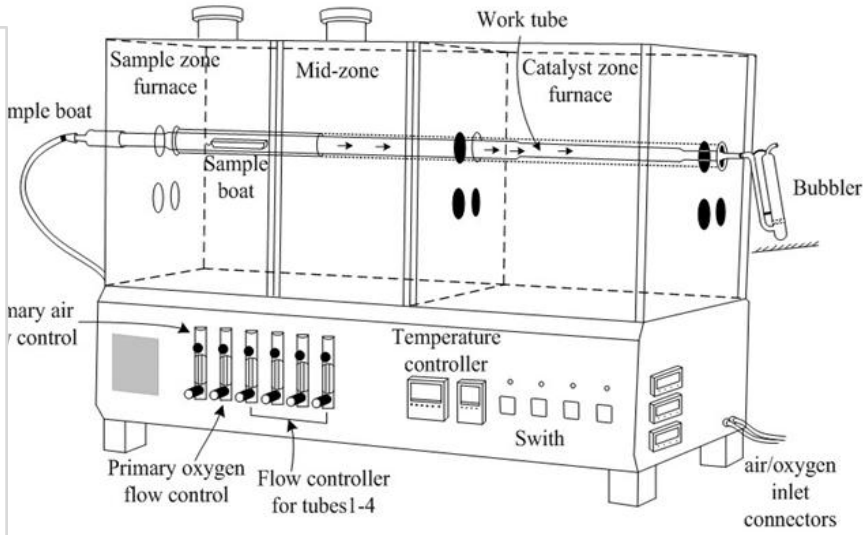
$$3I_2 + 6NaOH = 5NaI + NaIO_3 + 3H_2O$$

$$2I_2 + 2SO_3^{2-} + O_2 \rightarrow 4I^- + 2SO_4^{2-}$$

$$I^-(IO_3^-) + O_2 \rightarrow I_2$$

Separation of iodine from soil/sedimnt using combustion

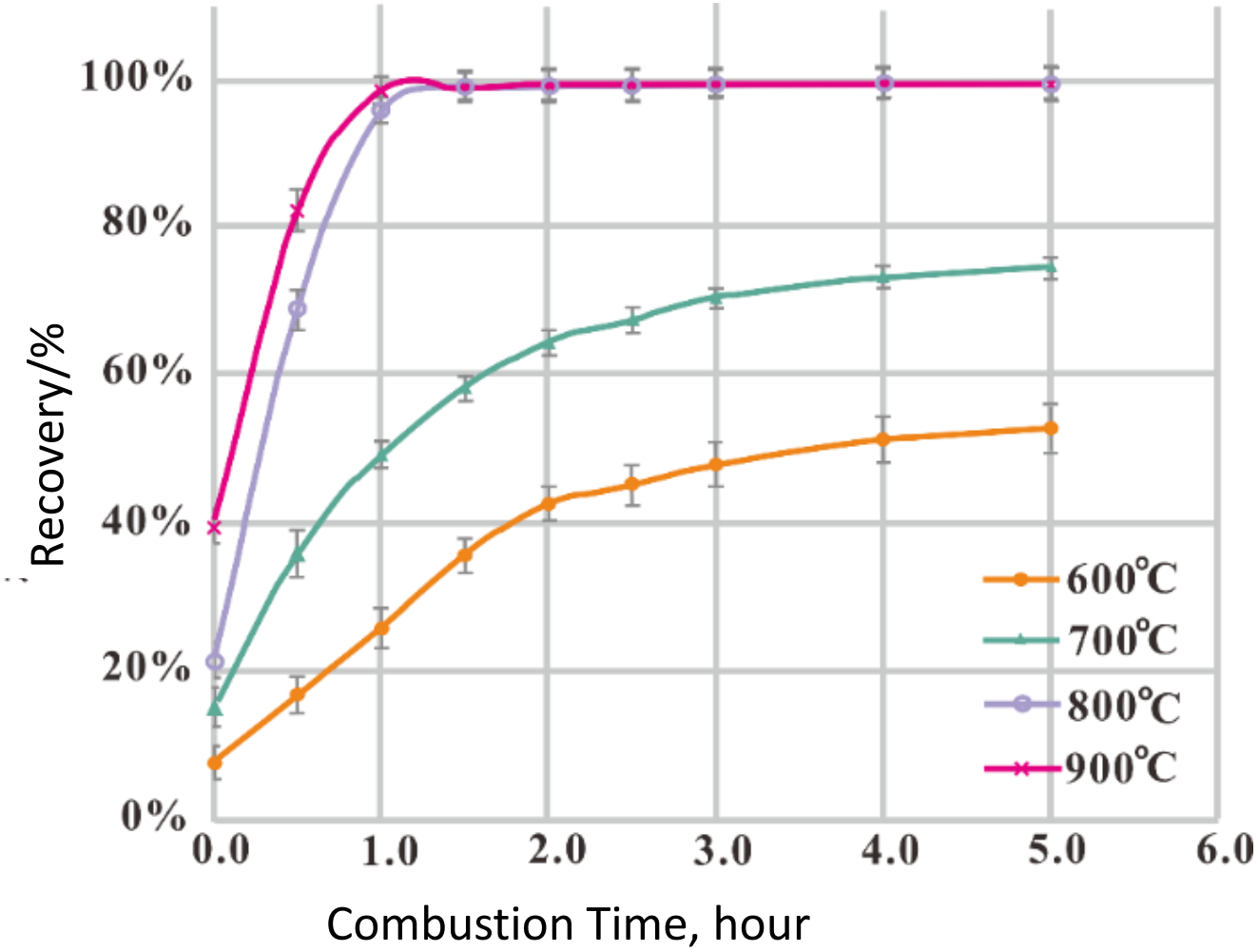


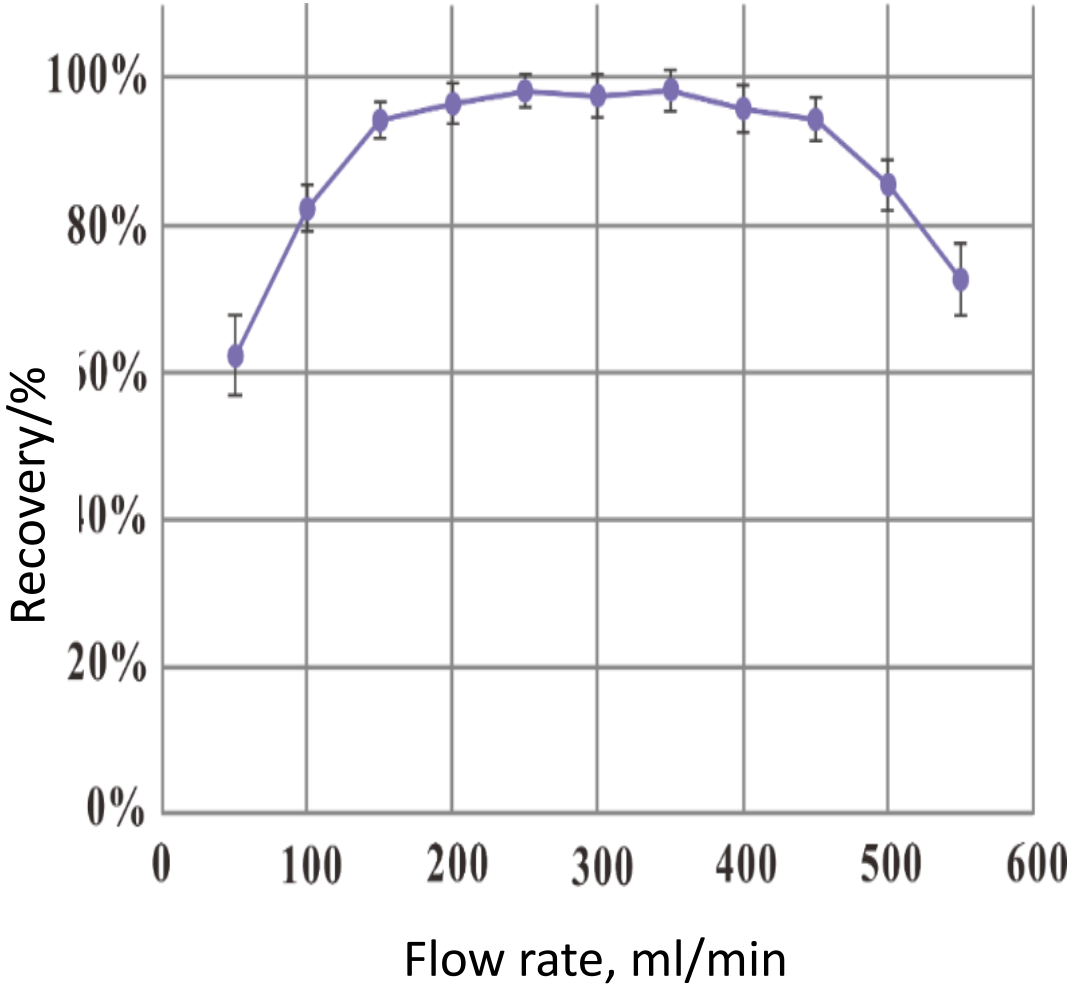


Temperarture rising, min

Zhang & Hou. JRNC, 2018

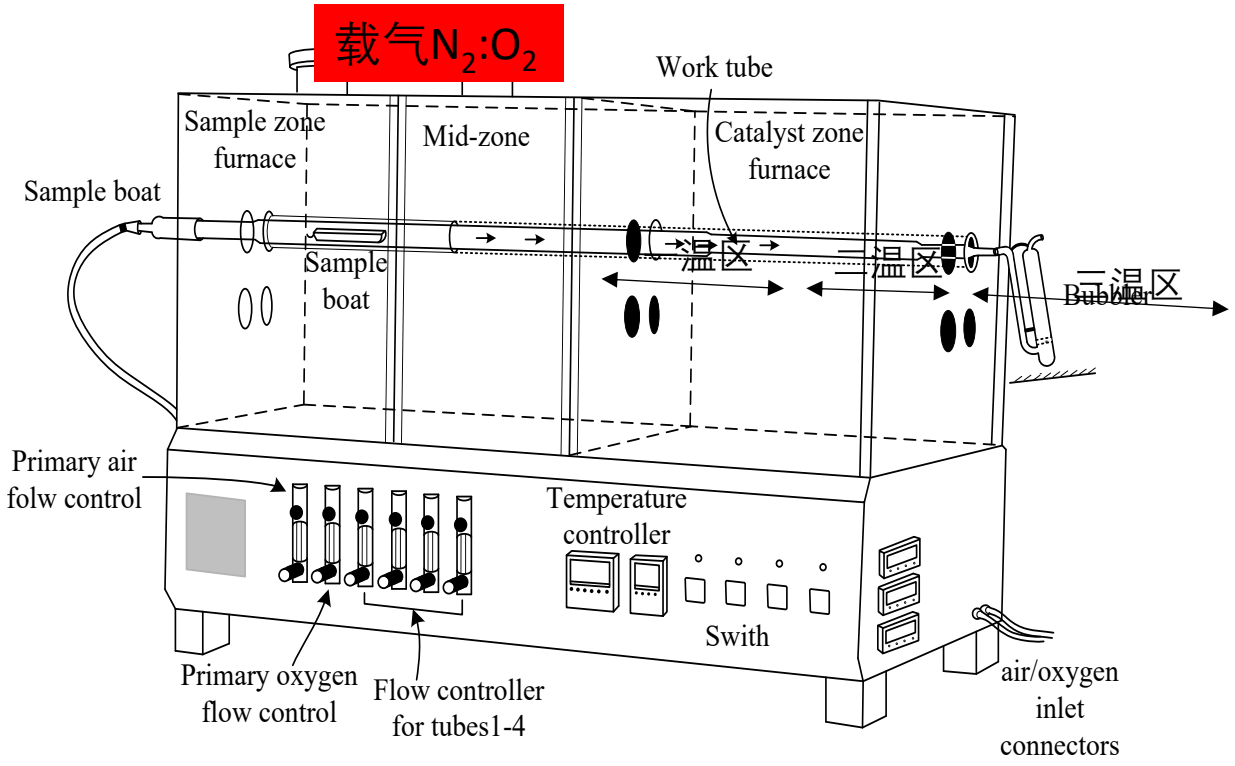
Separation of iodine from soil/sedimnt using combustion





Zhang & Hou. JRNC, 2018

Combiustion of vegetation sample for iodine separation



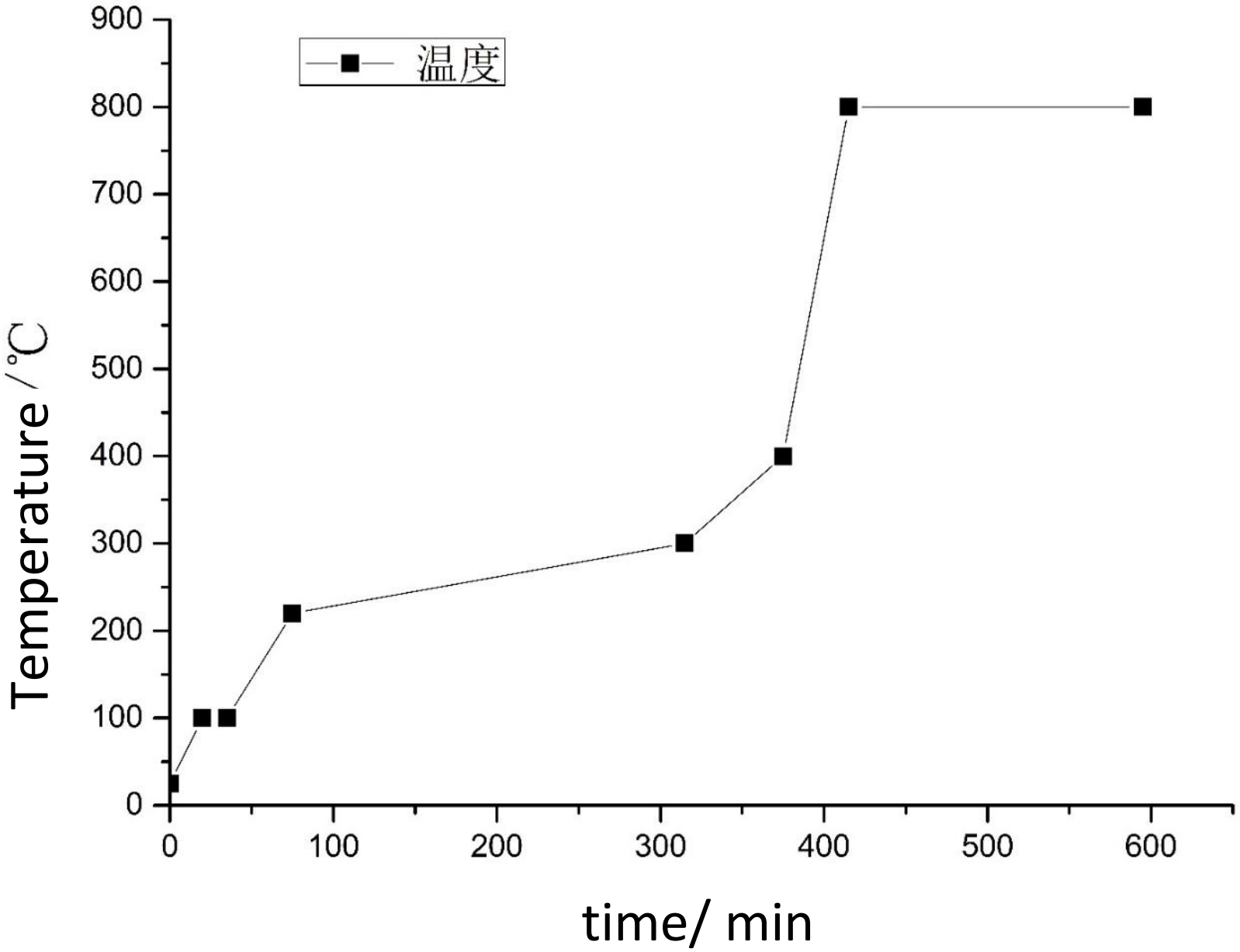
Experimental condition

Igniting point： 220-300℃

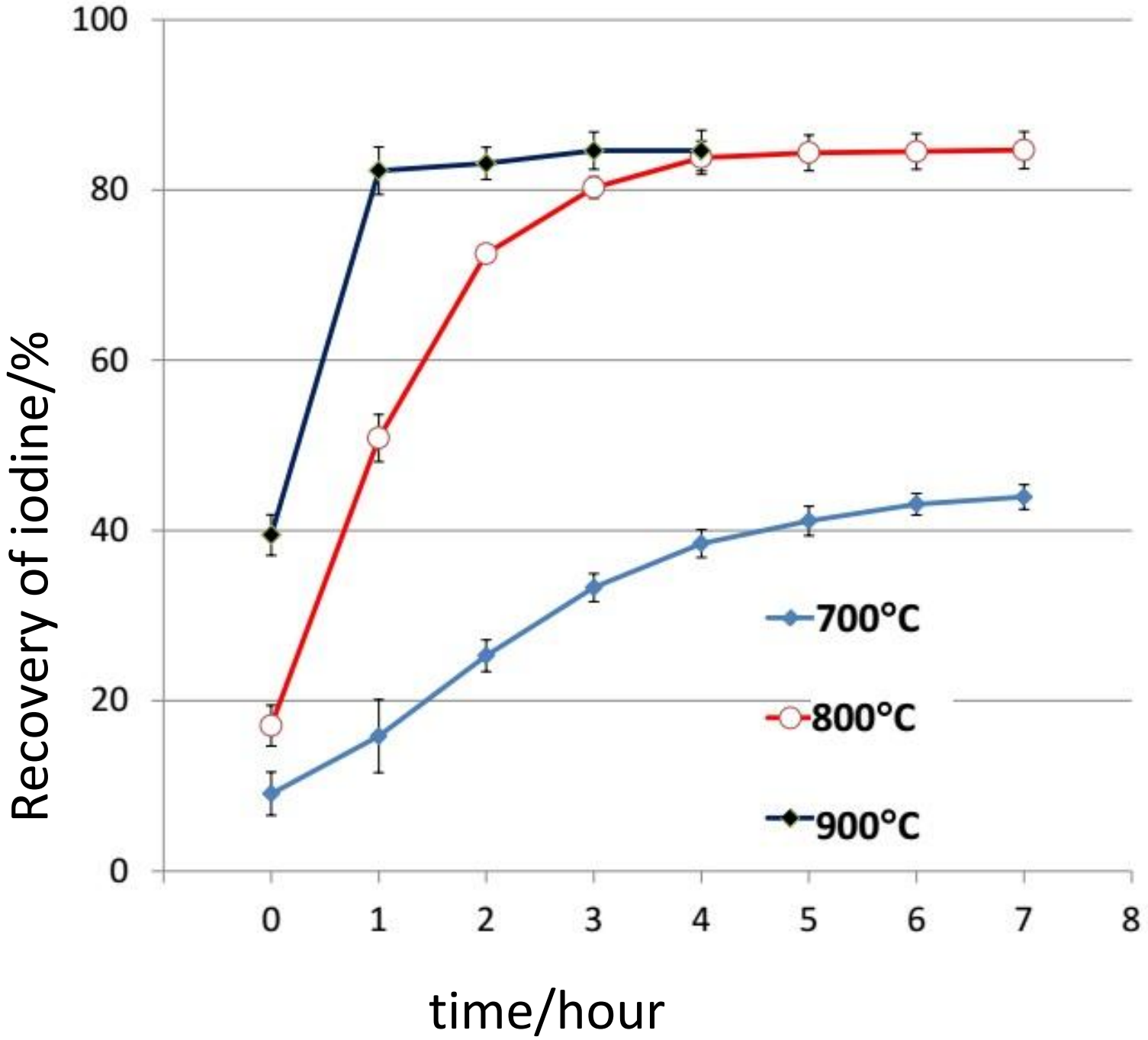
- Temperature ramp： 1-1.5℃/min

  Assistant gas O_2： N_2=1:2-1:3，
- Gas flow rate： 100-200ml/min
- Temperature in Zone 3 : :900℃
- Mass of sample: 5-10 g

Temperature ramp protocol

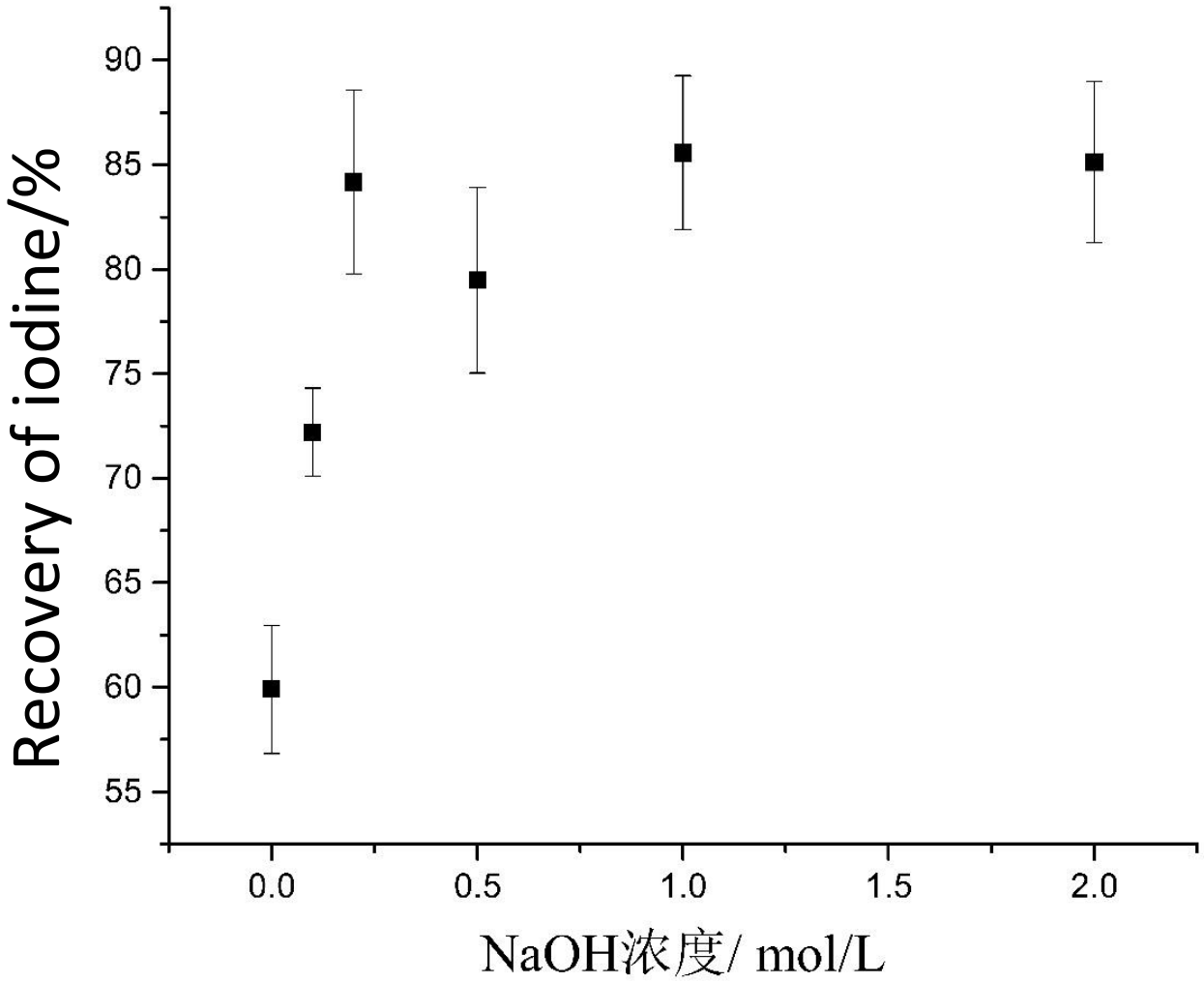


Influence of temperature and duriation

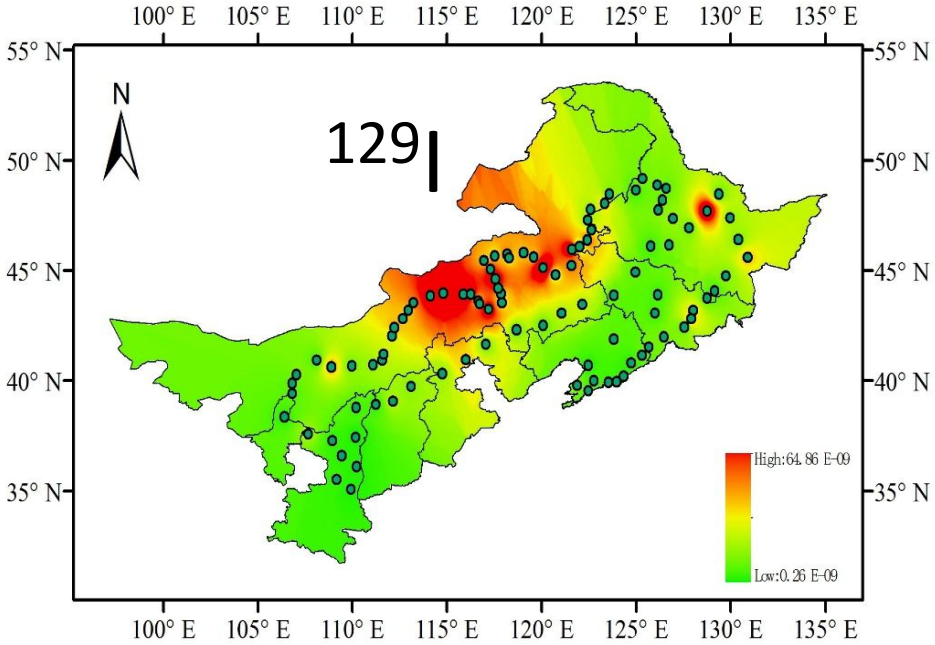


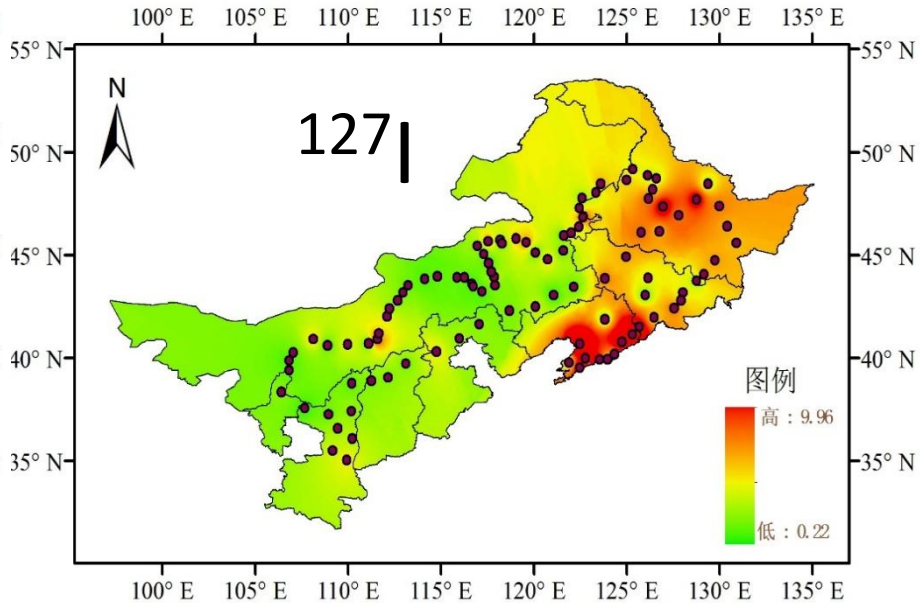
Trapping solution

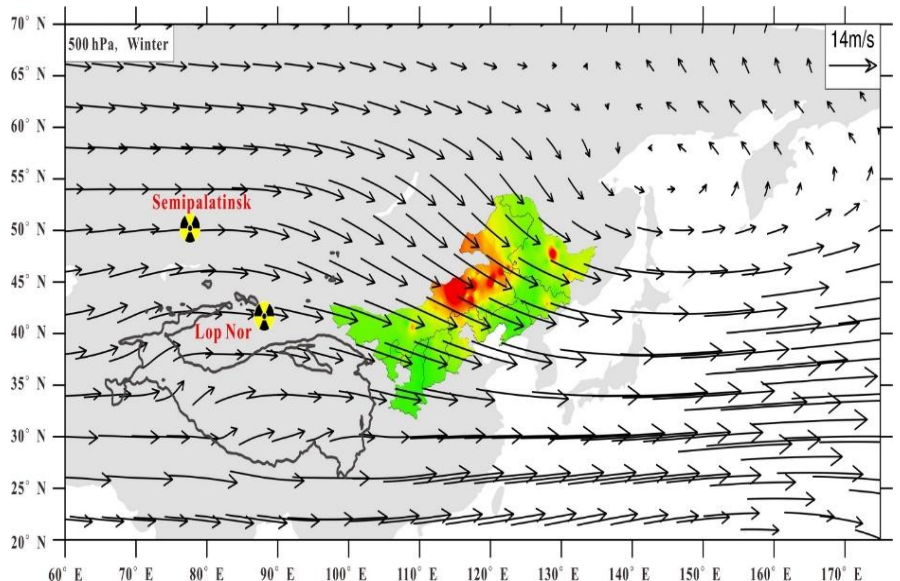
NaOH
– $NaHSO_3$ (0.05M)

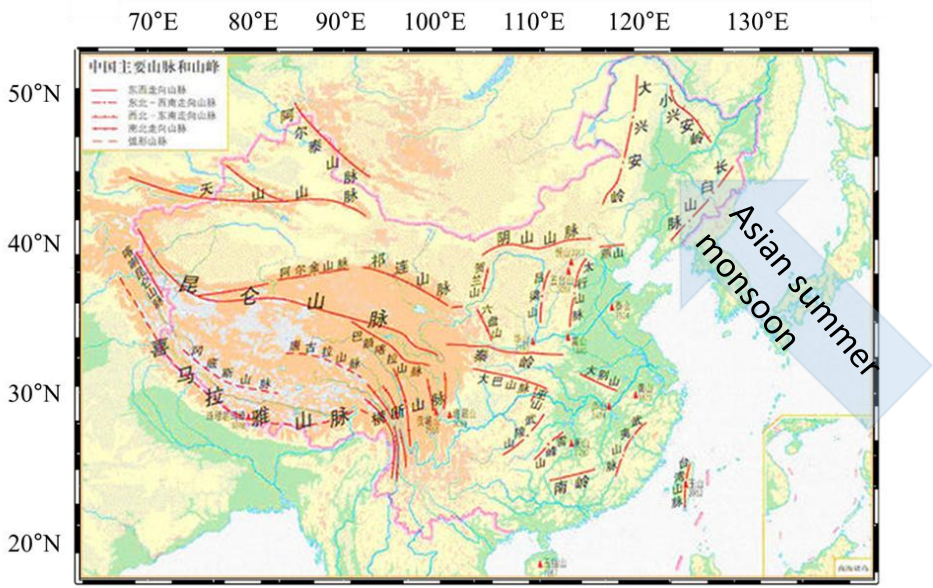


^{129}I in surface soil in Northeast China





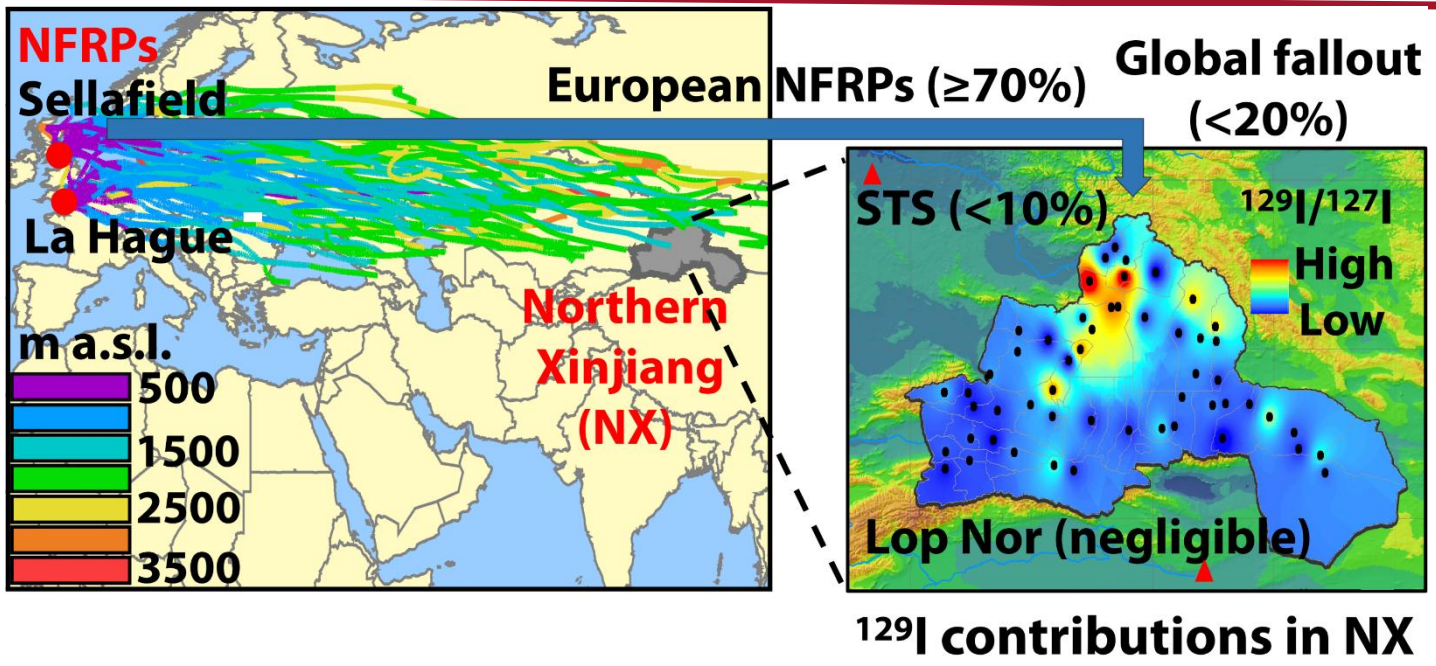


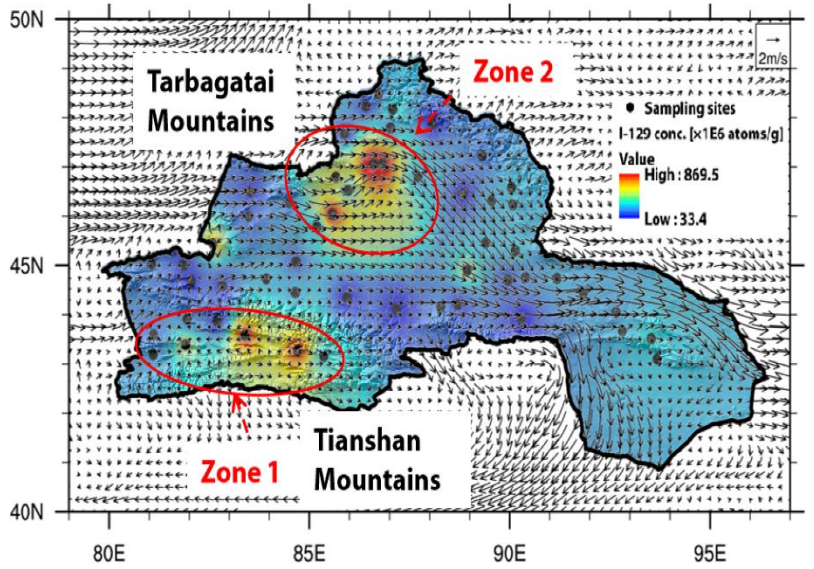


- **Different distribution of ^{129}I ad ^{127}I**
- **The dominant westward wind pass through the Semipalatinsk test site and arid area, transport ^{129}I to east**
- **The topography of mountains and vegetation coverage make ^{129}I deposited and reserved in this region**

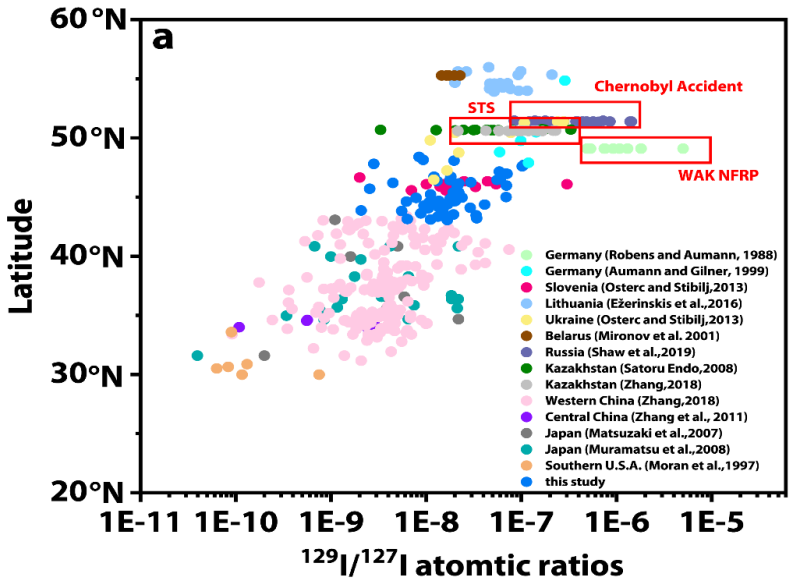
Wang, Hou, et al. STOTEN, 2024

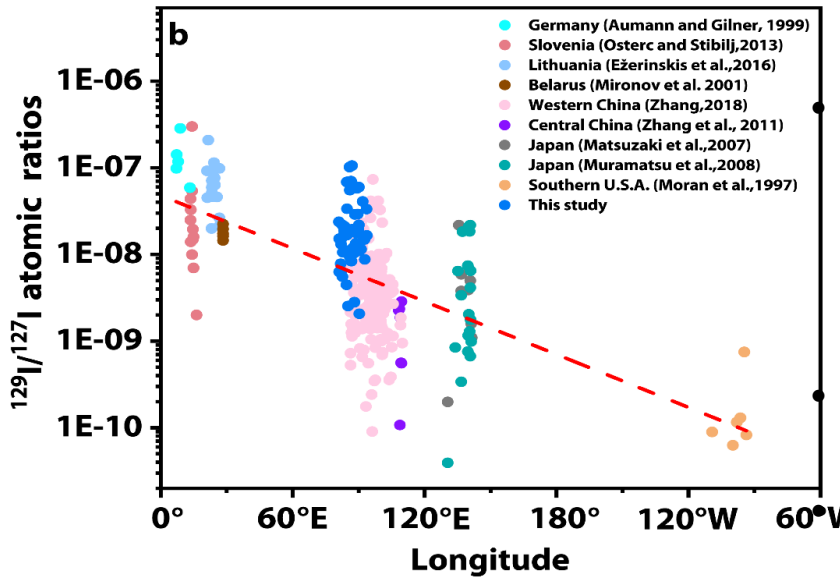
^{129}I in surface soil in the Northwest China





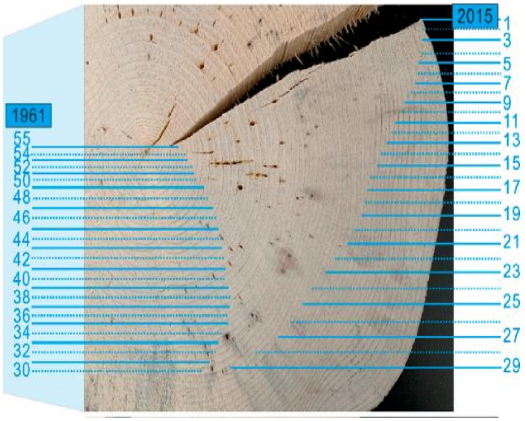
- ^{129}I in North China mainly originated from the European reprocessing plant through re-emission of marine discharged ^{129}I (>70%) driven by westlines.
  Global fallout (<20%) and regional deposition of wespons tests in Semiplatinsk (<10%) also contributed.
  No significant contribution from nuclear test in Lop Nor site.
  Topography dominate the transport pathway.

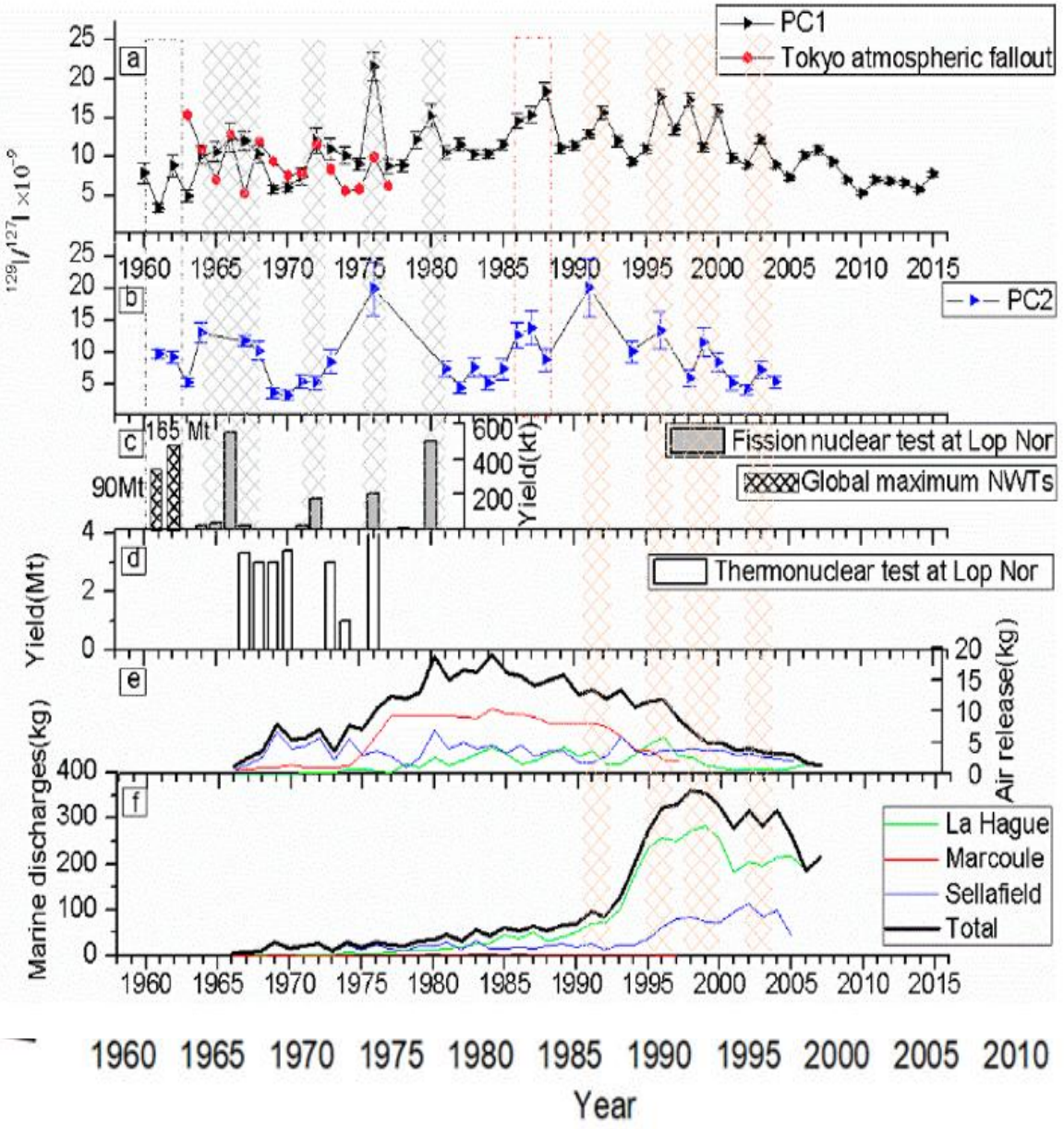




Liu, Hou, et al. ES&T, 2023, 57:10070-10078

Variation of $^{129}I/^{127}I$ in tree rings from Northwest China (Qinghai)

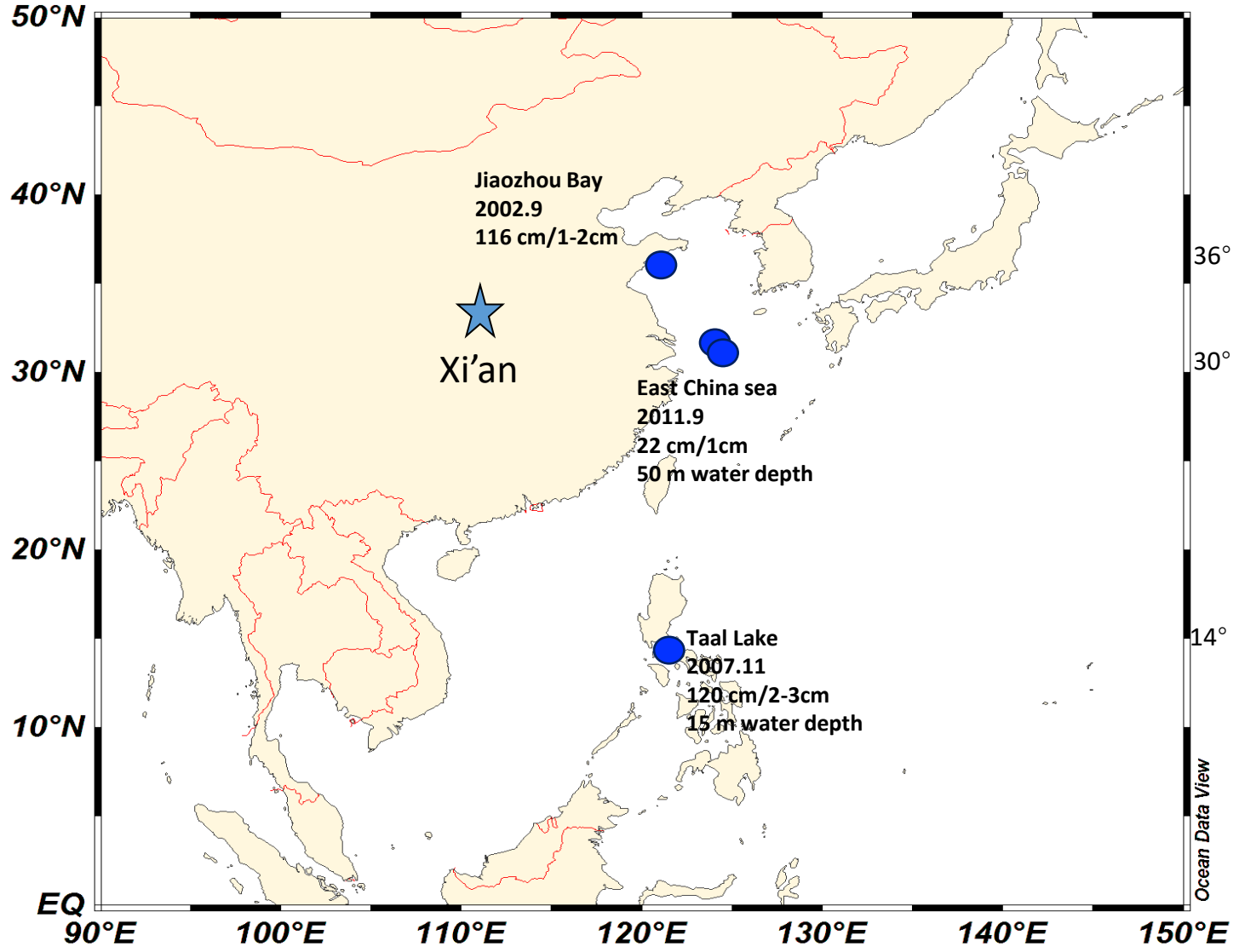




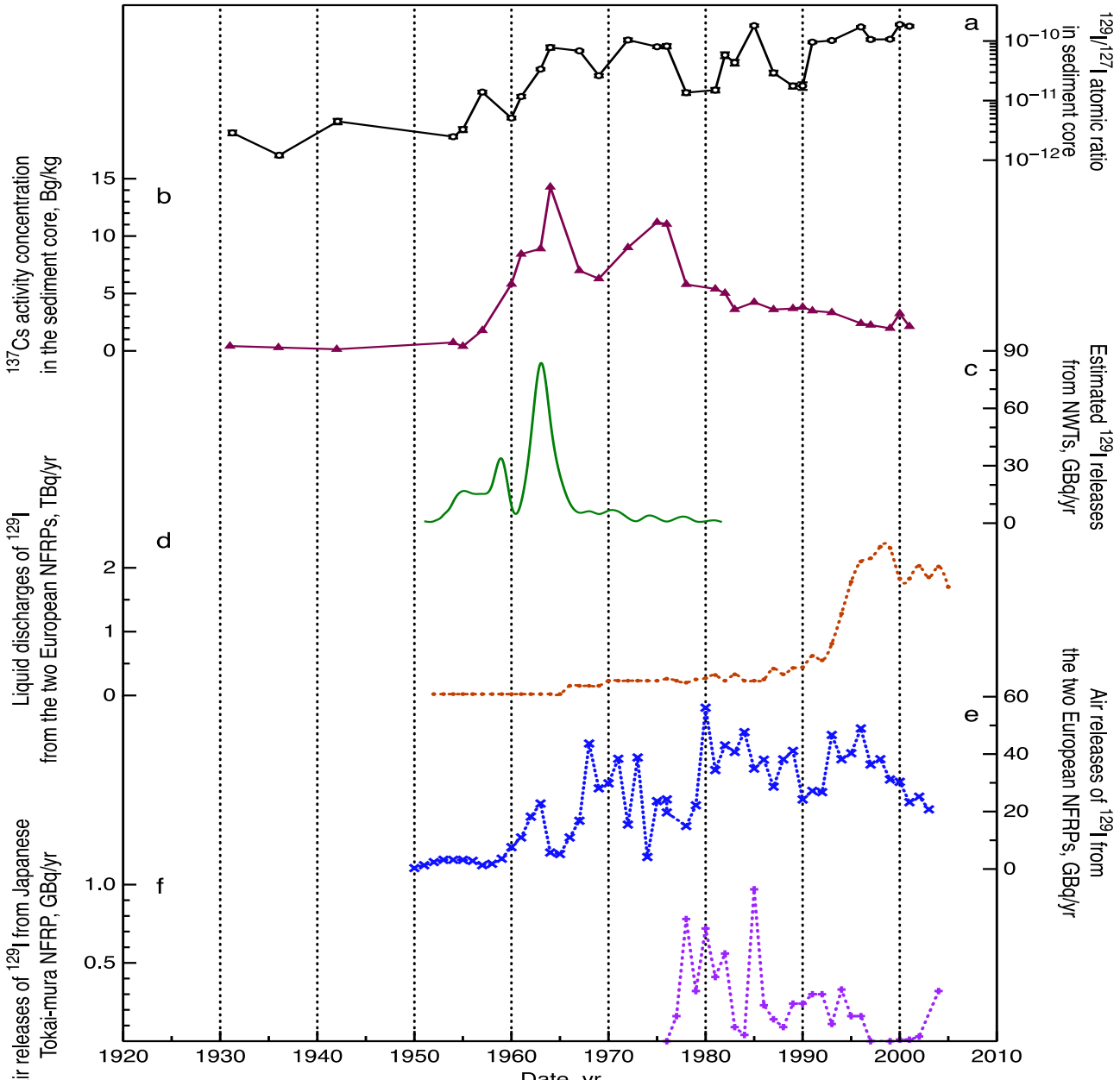
- **Nuclear weapons tests including Chinese tests were recorded in the tree ring.**
- **Constant high ^{129}I level was observed after 1980, matched well with the increased discharges of ^{129}I from European reprocessing plants.**

Zhao, Hou, Zhou, EST, 2019

Level of variation of ^{129}I in sediment cores at different latitudes in Asia



^{129}I profile in sediment core from Jiaozhou Bay, Yellow Sea

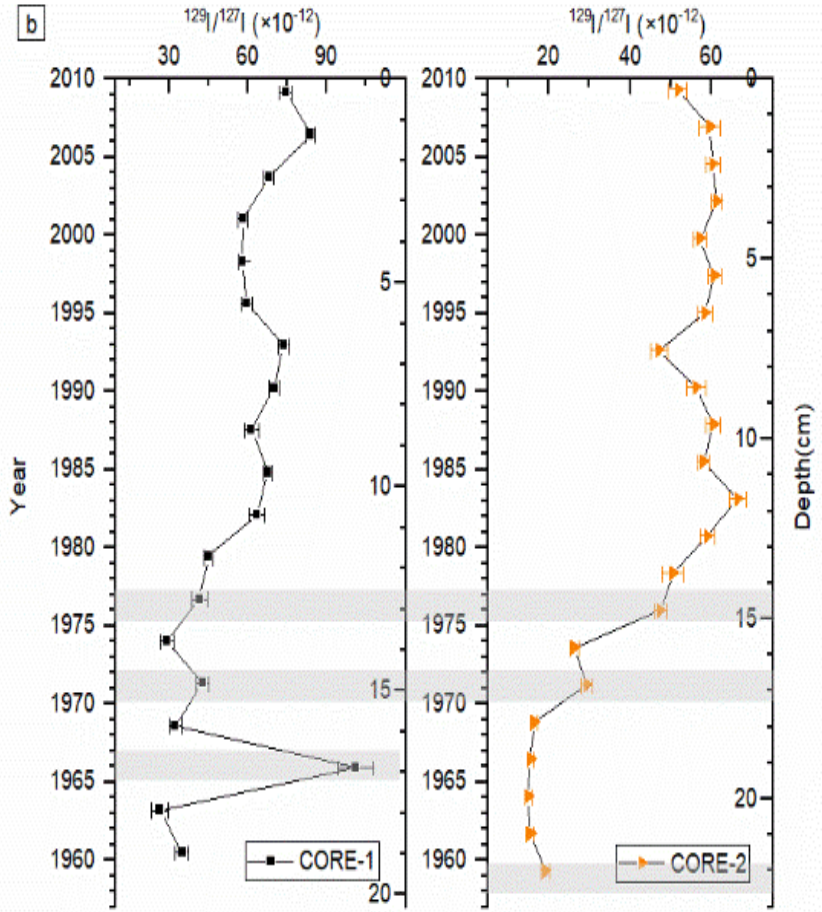


- European reprocessing releases dominates the present ^{129}I in North China.
- Re-emission from European seawater is an important source of ^{129}I in North China.
- Signals of weapons testing at PPG and Chernobyl accident signal was clearly recorded in the sediment core.

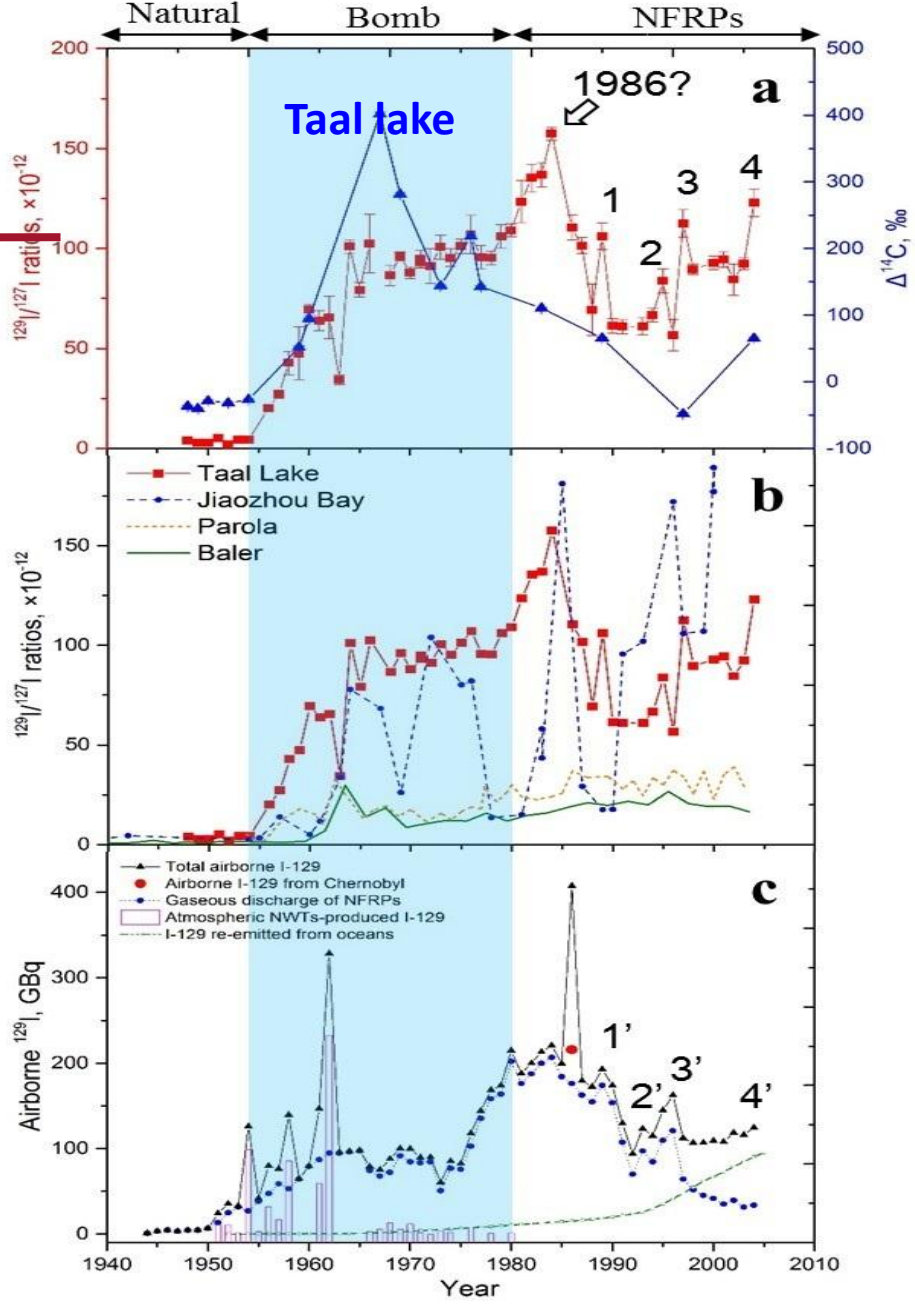
Fan, Hou, et al. JER, 2016

$^{129}I/^{127}I$ profile in sediment cores from the East China Sea and Taal lake, Philipines

East China Sea



Zhao, Hou, et al. Envir. Poll. 2019



Zhang, Hou, et al. Chemosphere, 2018

Thanks you for your attention！

9th International Conference on Environmental Radioactivity

ENVIRA 2027

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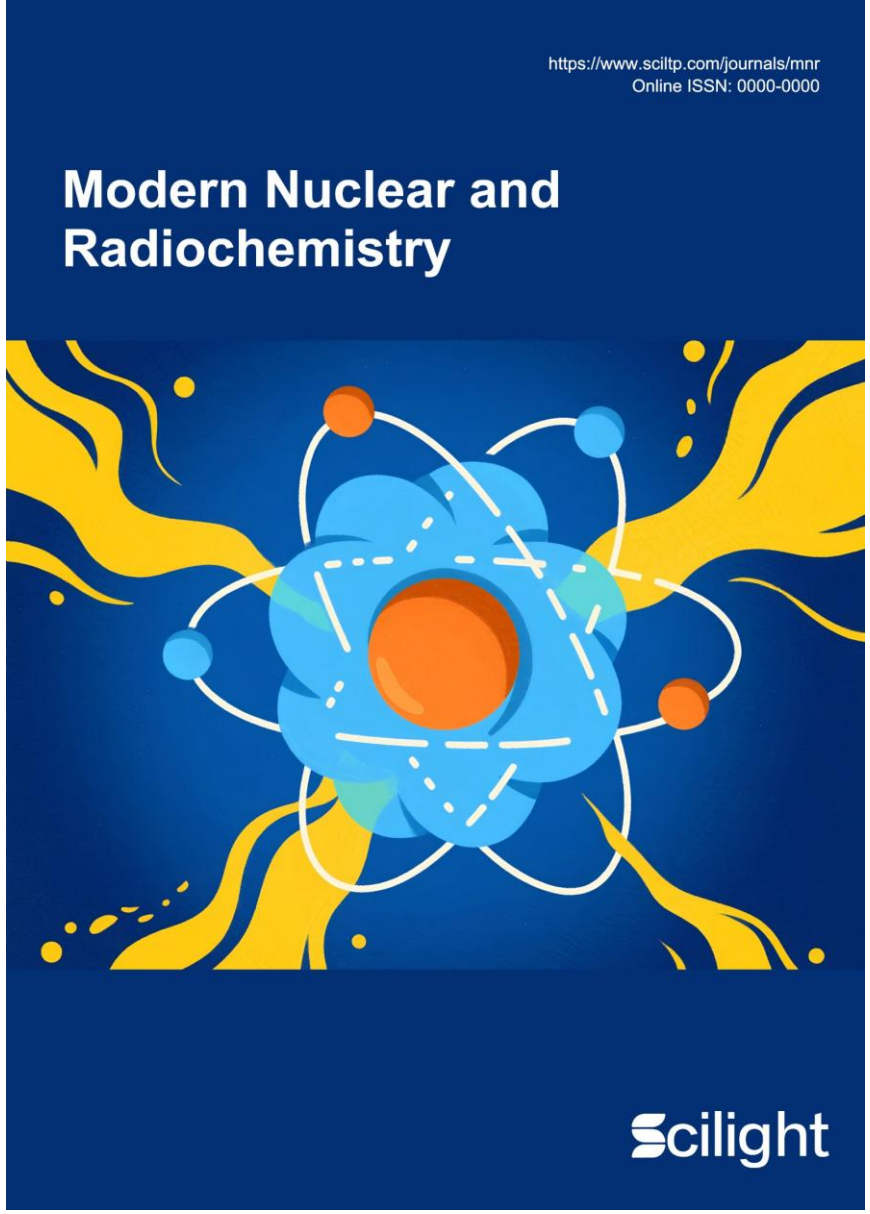

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