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SINCHRON
A NEW CHRONOMETER FOR NUCLEAR DATING

EPFL

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Radiochemical separation of Si-32 from proton-irradiated vanadium: Towards an accurate half-life determination

Virtual Conference on Applied Radiation Metrology (vCARM)
Wednesday, 24th of November 2021 :: TrisKem User Group Meeting

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Agenda

Introduction	Results	Conclusion
1	2	3
Slide: #1	**Slides: #2 - #11**	**Slide: #12**

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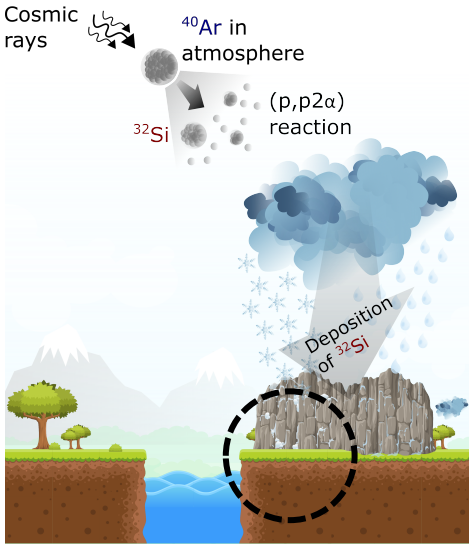
Introduction

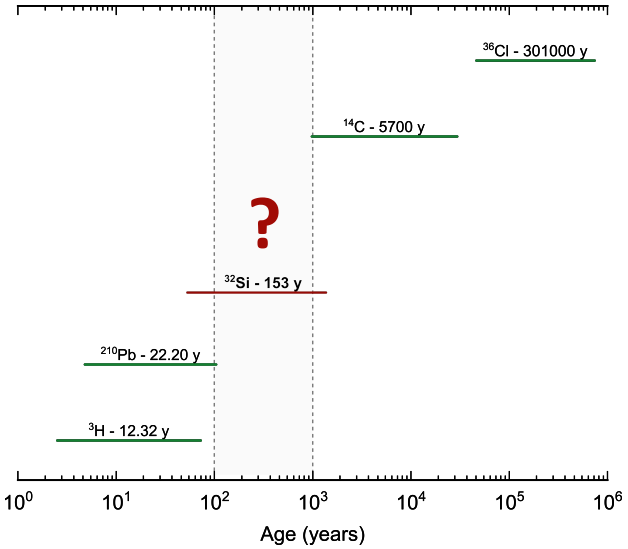
Radioactive silicon-32: Why is it of great interest?



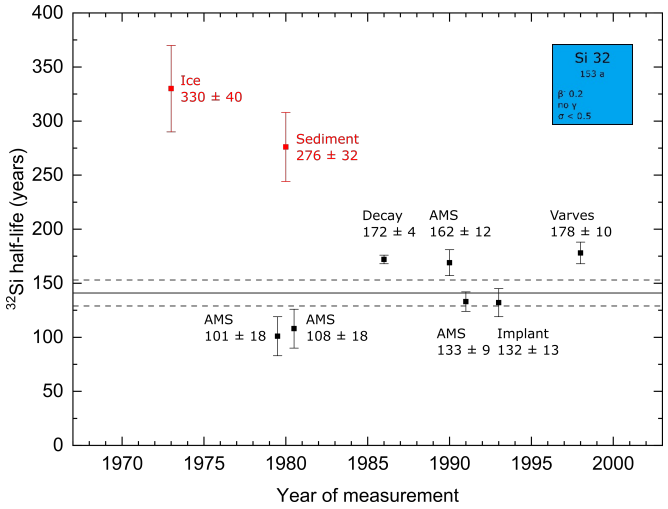
- **Cosmological** origin
- **Deposition**: terrestrial sediments, snow, and ice

→ **Radiometric dating**[1]

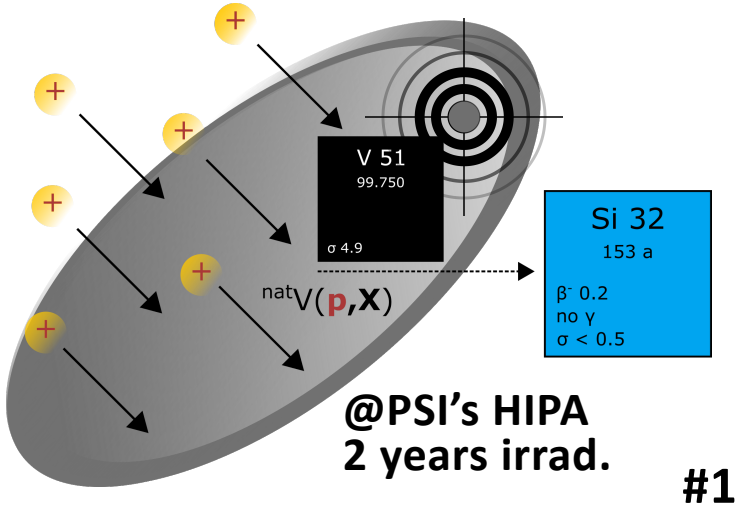
= *very little sample material:* ***countable atoms***



Challenge: Lack of Sample Material

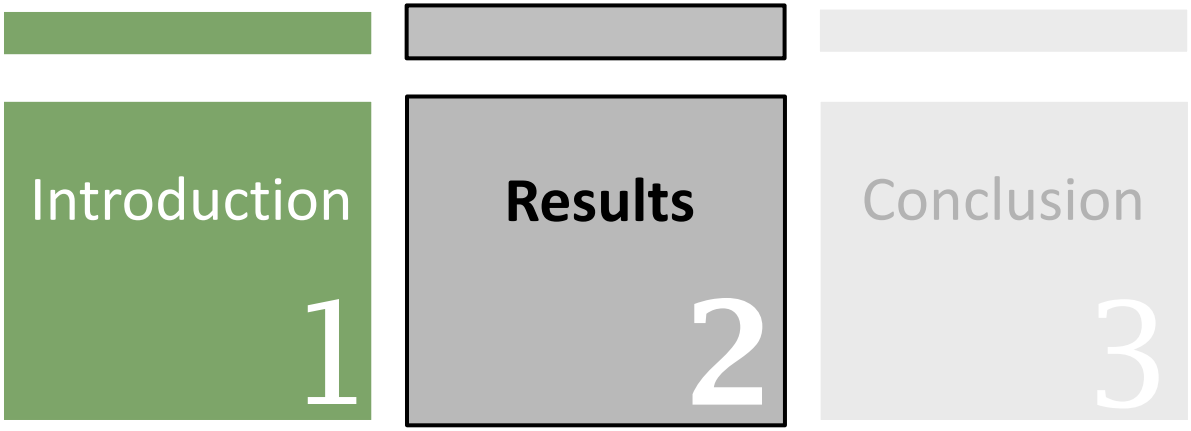


Artificial Production: V Target



@PSI's HIPA
2 years irrad.

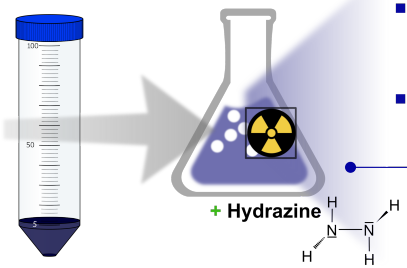
Agenda



Slide: #1 **Slides: #2 - #11** **Slide: #12**

Results

Dissolution of an p-irradiated vanadium disc (m(disc) = 400 mg) in 2.5 mL 8M HNO_3 / 2.5 mL 8M HCl: **Initial vanadium solution**

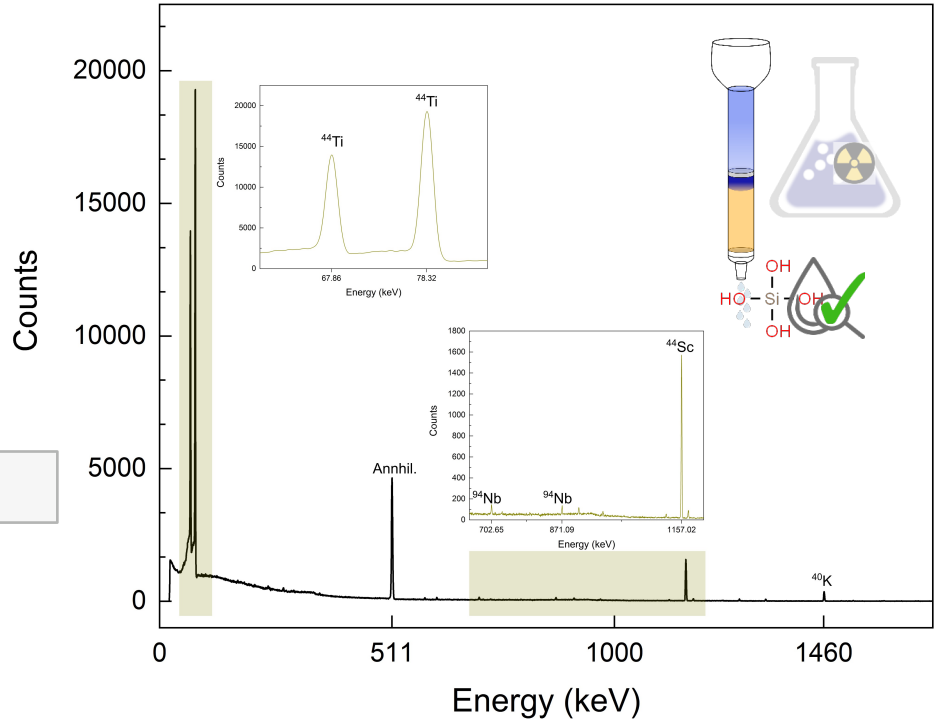


- Radioactive vanadium solution
- Dilution with H_2O to set pH to ~ 0.8 ($c(H^+)$ = 0.15M)
- Vanadium as $V^{+IV}O^{2+}$ and silicon as $SiO_{2\,(s)} + 2\,H_2O \rightleftharpoons Si(OH)_{4\,(aq)}$

+ Hydrazine

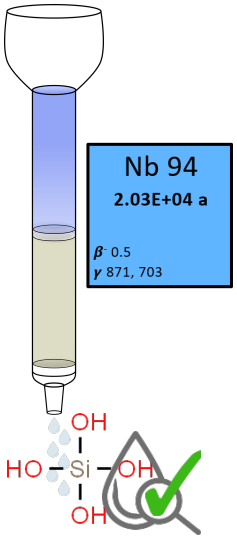
Developed to process (!) 150x V-discs

2. Ion Exchange Chromatography: BULK

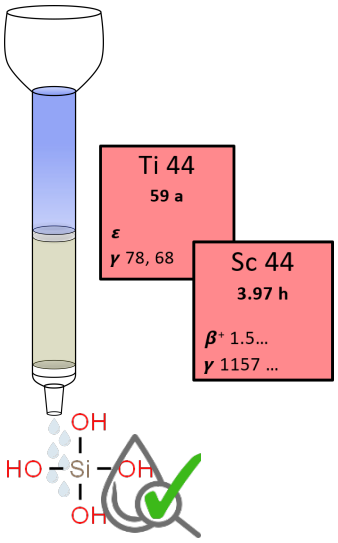


3. Extraction + Chelating Resins: PURIFICATION

Monophos



LN

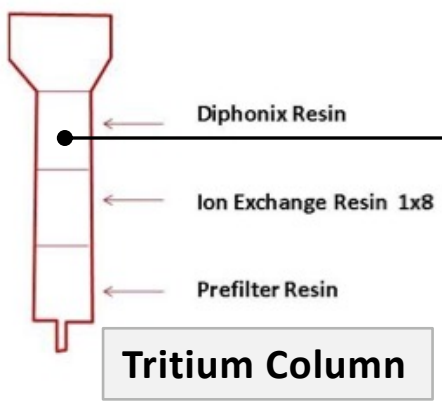


Key aspects for the reliable separation scheme:

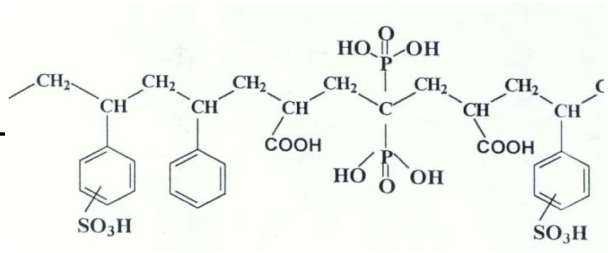
- ✓ **Remove majority** of the **matrix** (=vanadium)
- ✓ Specifically **targeting impurities**: specific resins

  → **Purification** process

Results



Tritium Column



Polymeric support: functionalized w/ **di**phosphonic and sulphonic acid groups.

TRISKEM
Expertise in Separation Chemistry

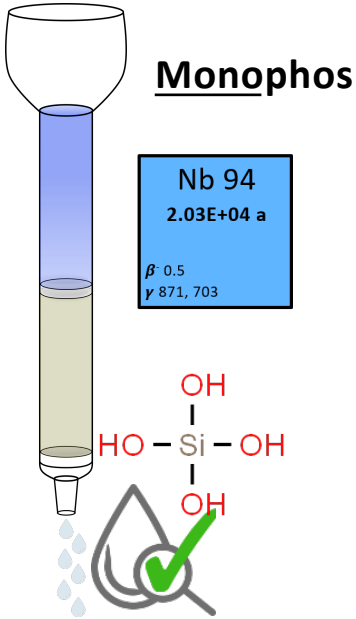


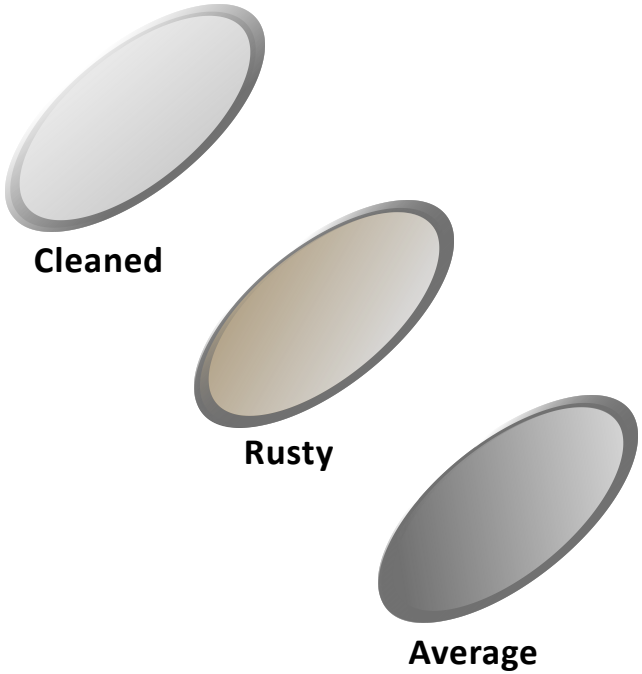
Table 1: Radionuclide removal of samples from a pressurized water reactor.

Isotope	Ox. State	A before Column (Bq/L)	A after column (Bq/L)
Cr-51	+III, +IV	2900	**< Detection Limit (< DL)**
Mn-54	+II	518	
Co-58	+II	4740	
Fe-59	+II, +III	**109**	
Co-60	+II	392	
Sn-113	+IV	230	
Nb-95	+V	**4220**	
Zr-95	+II, +IV	**2210**	
Cs-134	+I	1120	
Cs-137	+I	1320	

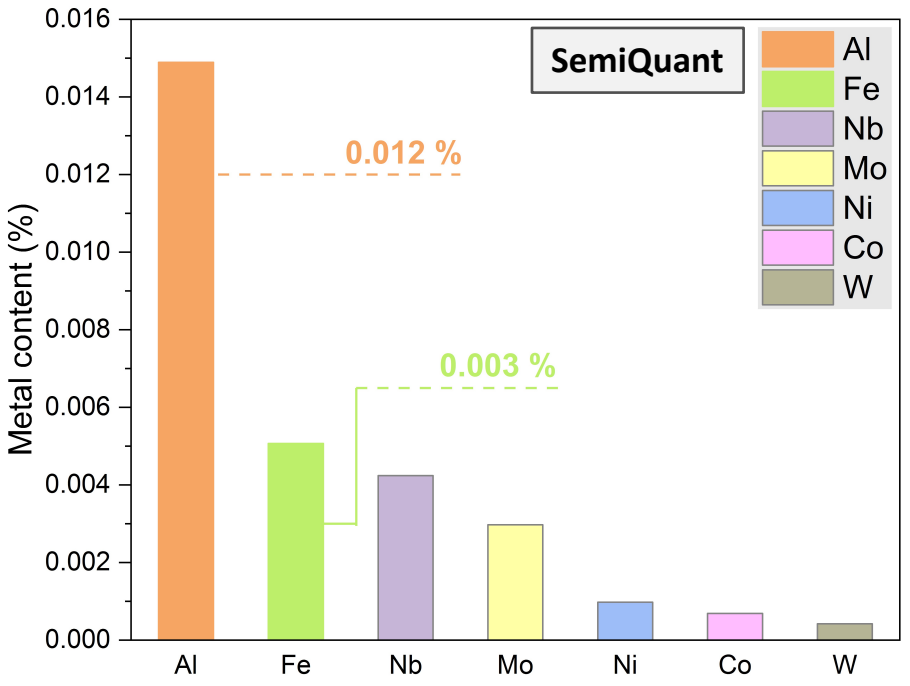
Results

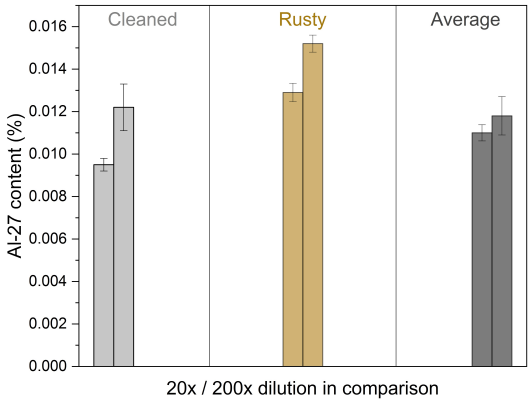
EPFL Valais | Wallis @ISIC-MSEAP

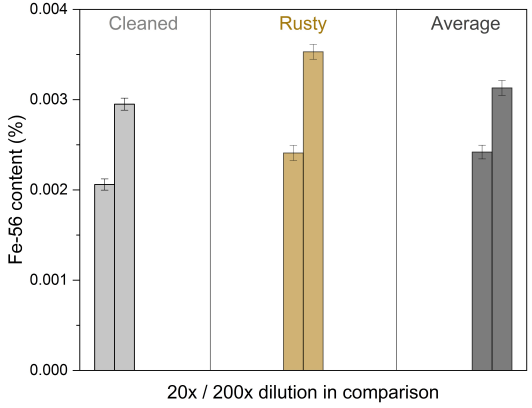
EPFL Thanks to Dr Natalia Gasilova



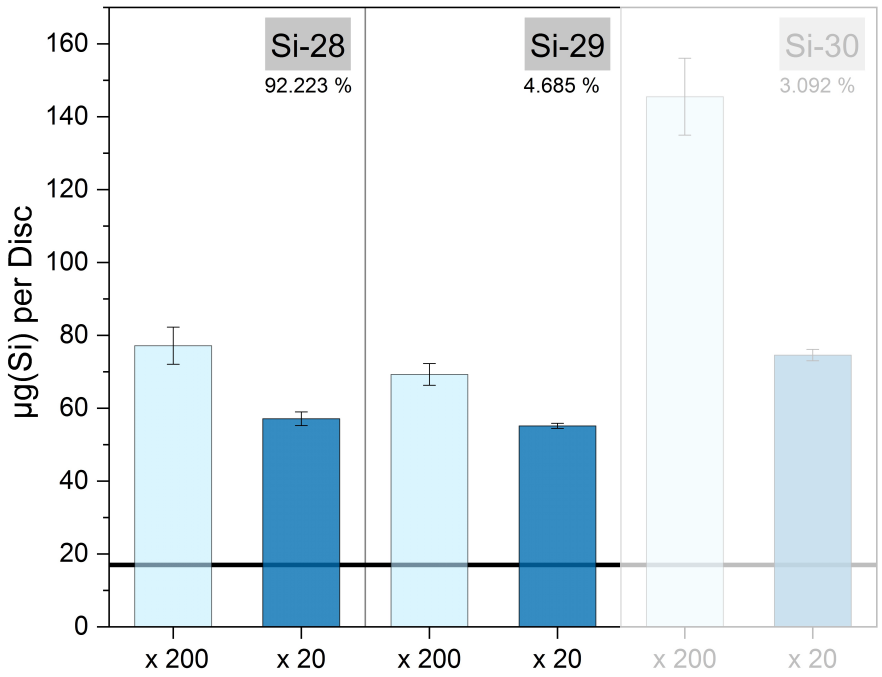
- 1mm thick, Ø = 9 mm
- m(disc): ≈ 400 mg







Results



Si 28	Si 29	Si 30
92.223	4.685	3.092
σ 0.17	σ 0.12	σ 0.107

Dilution	Si-28 (µg)	Si-29 (µg)	Average per disc (µg)
x **200**	77	69	73
x **20**	57	55	56
			64.5

Interferences

^{28}Si: $^{14}N_2^+$ and $^{12}C^{16}O^+$

^{29}Si: $^{14}N^{15}N^+$. $^{14}N_2{}^1H^+$. $^{13}C^{16}O^+$. $^{12}C^{17}O^+$. $^{12}C^{16}O^1H^+$

^{30}Si: $^{15}N_2^+$. $^{14}N^{15}N^1H^+$. $^{14}N^{16}O^+$. $^{12}C^{18}O^+$. $^{13}C^{17}O^+$. $^{13}C^{17}O^+$. $^{13}C^{16}O^1H^+$. $^{12}C^{17}O^1H^+$. $^{14}N_2{}^1H_2^+$. $^{12}C^{16}O^1H_2^+$

Results

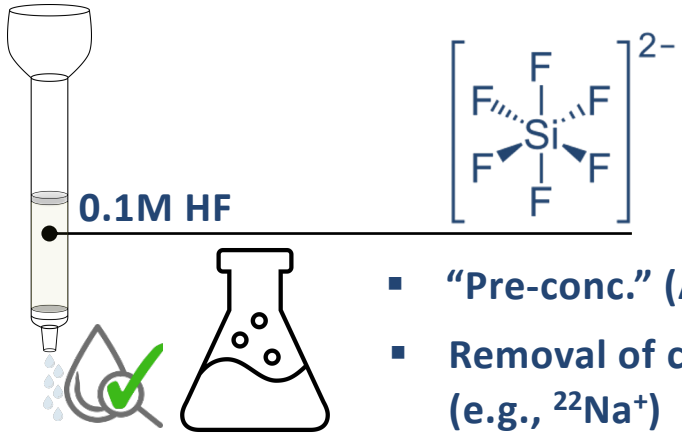
4. Remove gaseous radioactive elements

H 3	Ar 39	Ar 42
12.312 a	269 a	32.9 a
β^- 0.018	β^- 0.6	β^- 0.6
no γ	no γ	no γ

Evaporation to dryness (PTFE dishes)

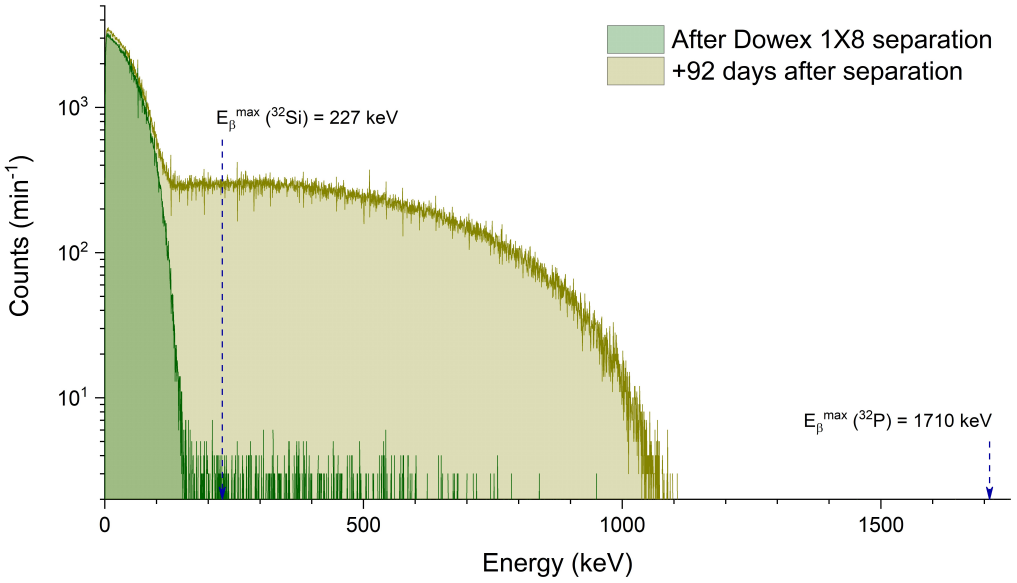
Recovery of SiO_2 with hydrofluoric acid (HF)
Each V-disc => one fraction (20mL 0.1M HF)

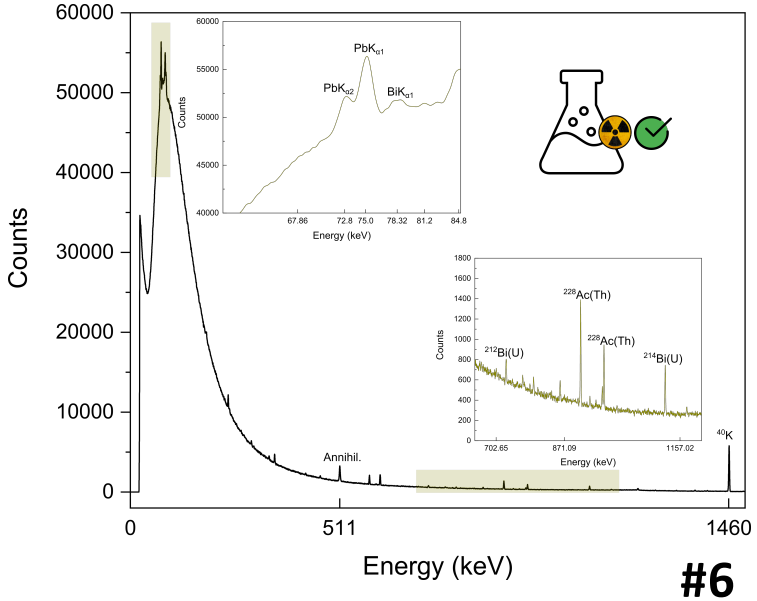
5. Ion Exchange Chromatography: Final



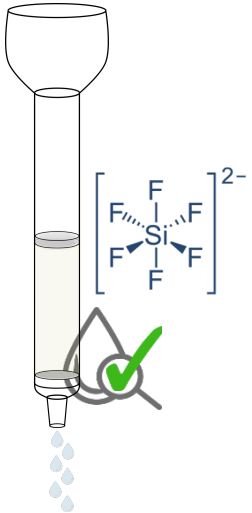
- "Pre-conc." (A(^{32}Si))
- Removal of cations (e.g., $^{22}Na^+$)

QC in-house: Liquid Scintillation Counting (LSC) & (repeat.) long-term γ-measurements

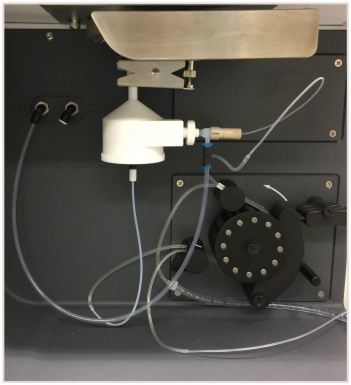




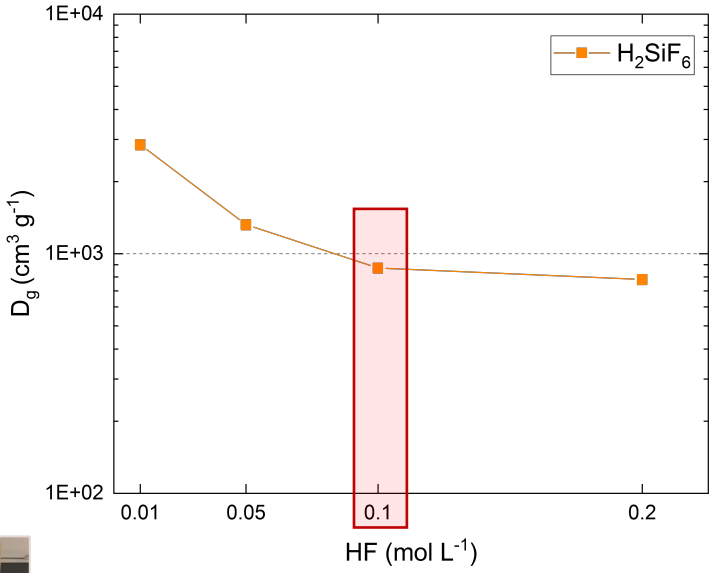
5. Ion Exchange Chromatography: K_d studies



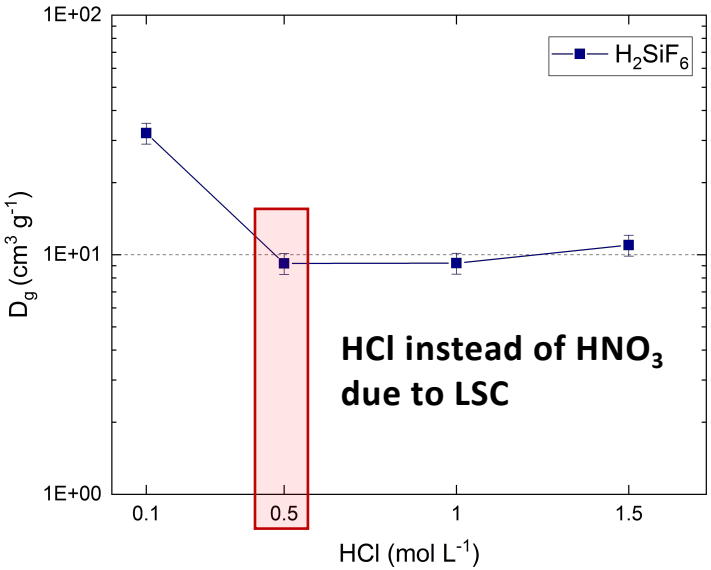
✓ Si K_d studies



Retention



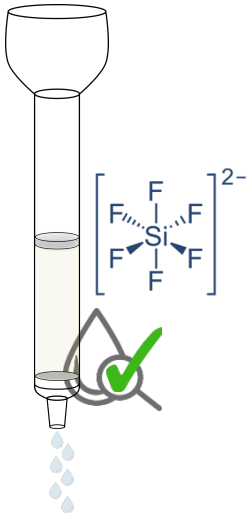
Elution



Chosen Experimental Conditions

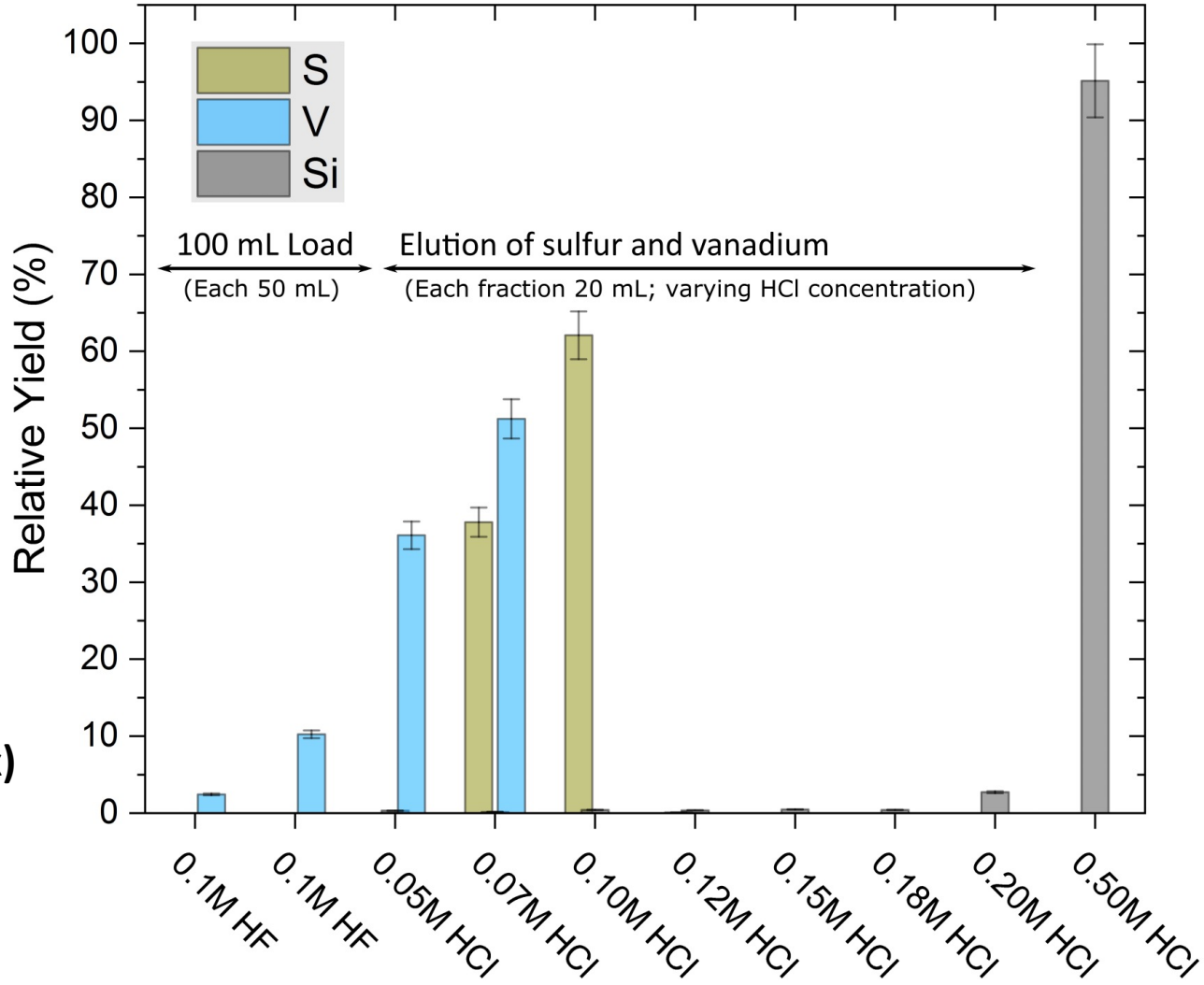
Agilent 5110: PTFE-sample introduction (+PTFE torch)

5. Ion Exchange Chromatography: Removal of matrix (=^{nat}V) trace amounts + sulfur treatment

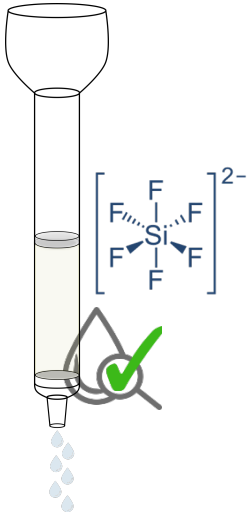


✓ Si K_d studies

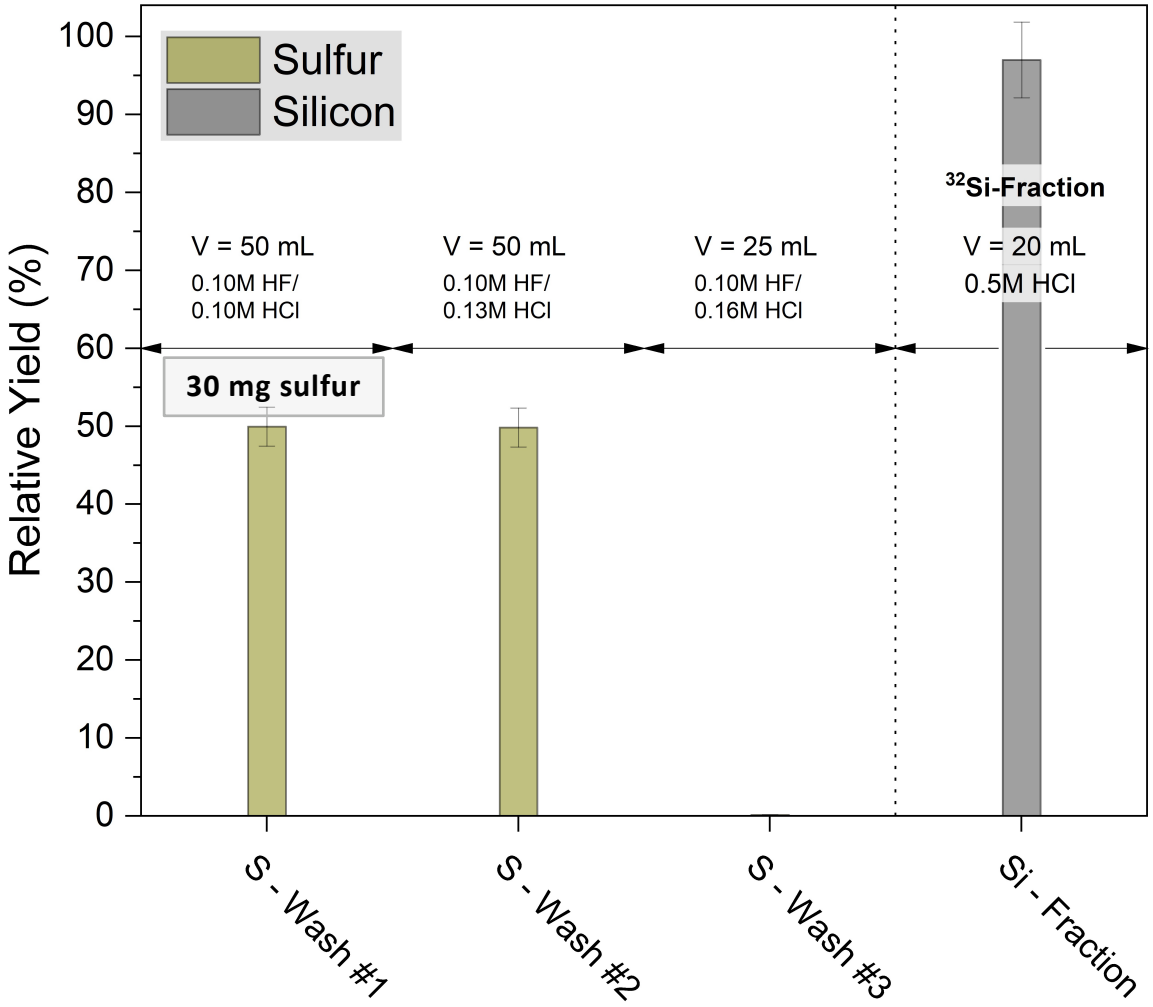
✓ **Removal of trace impurities (= Matrix)**



5. Ion Exchange Chromatography: Addition and subsequent removal of sulfur



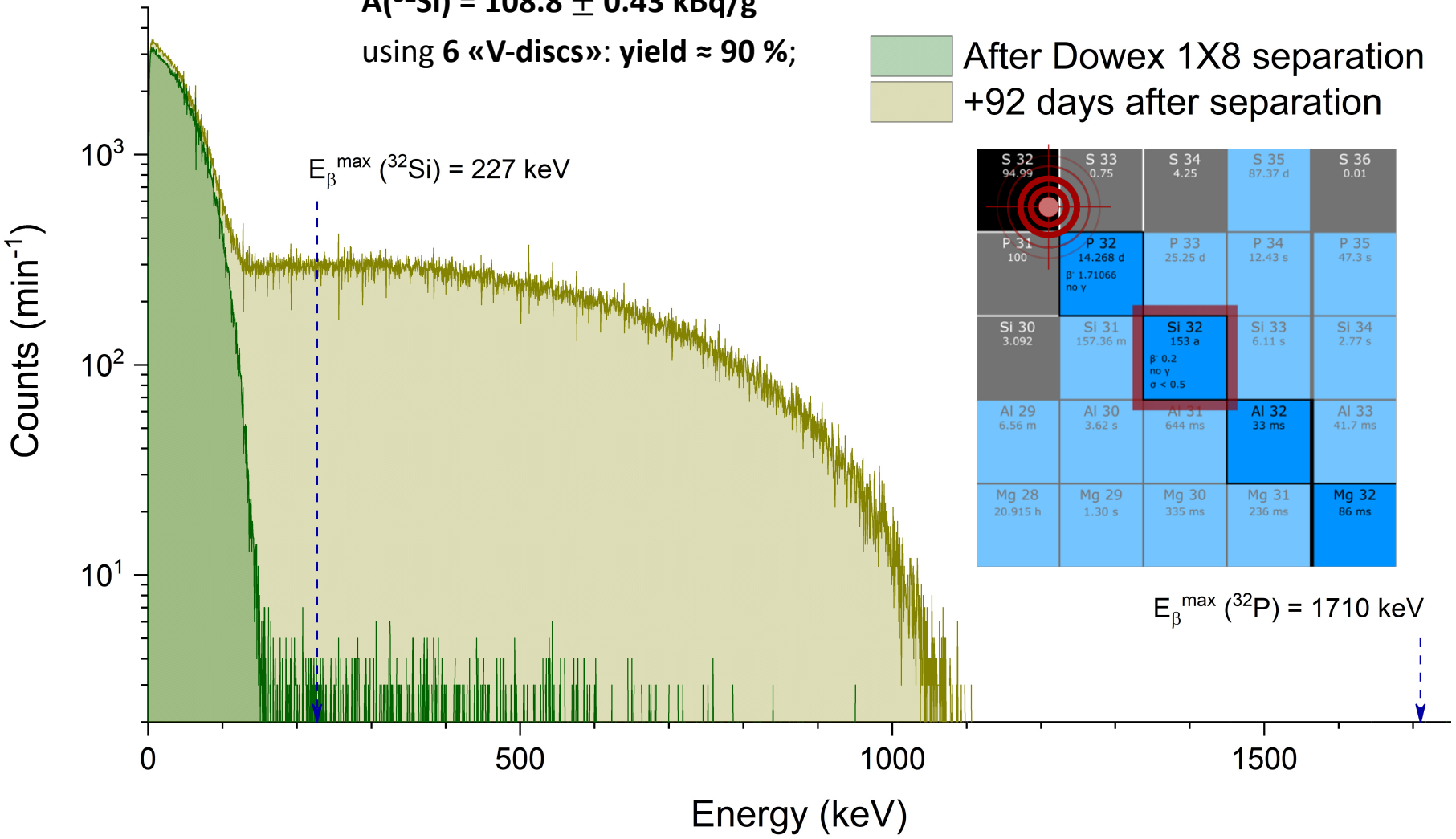
- ✓ Si K_d studies
- ✓ Removal of trace impurities (= Matrix)
- ✓ **Nat. isotopic abundance of S: if detected**



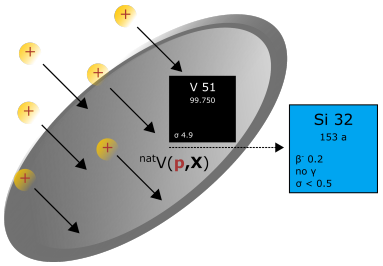
5. Ion Exchange Chromatography: Final ^{32}Si solution in 0.5M HCl

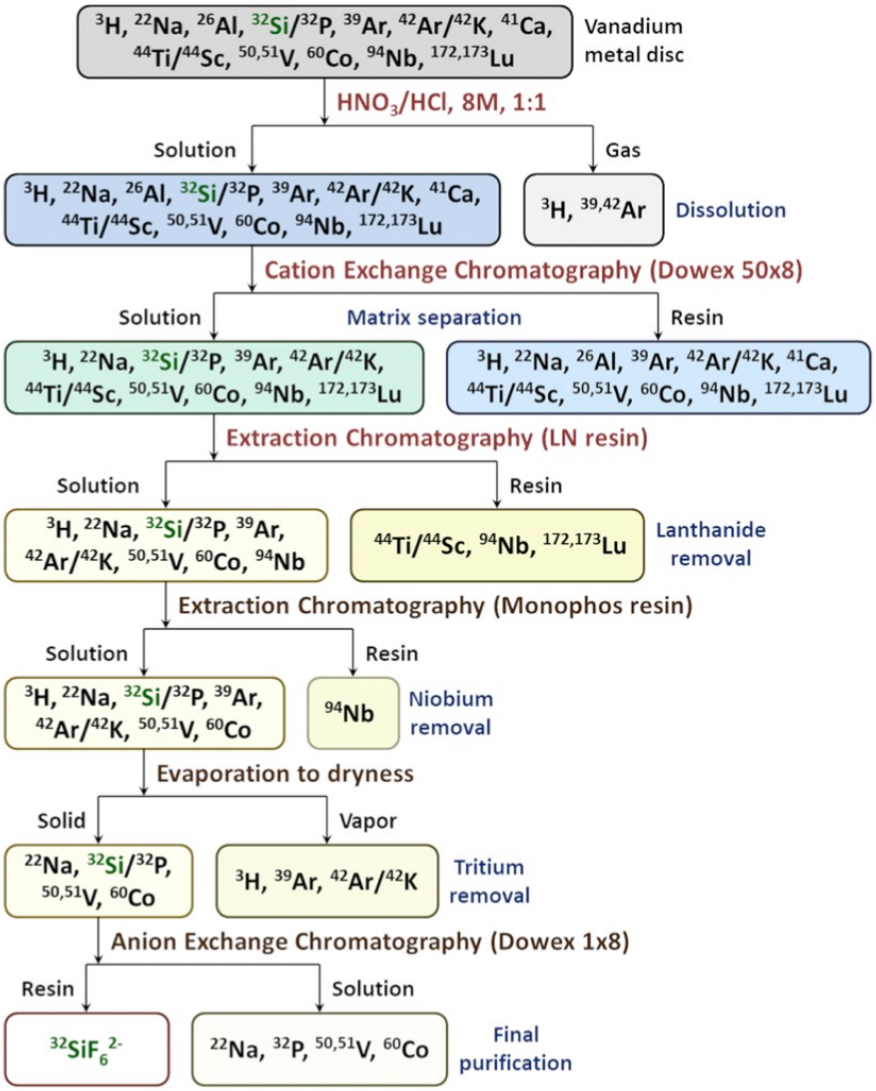
A(^{32}Si) = 108.8 ± 0.43 kBq/g

using **6 «V-discs»**: **yield ≈ 90 %;**



Results





0.5M HCl
^{32}Si solution

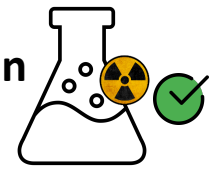


Figure 5: Step-wise separation of nca ^{32}Si from proton-irradiated vanadium matrix.

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Agenda

Slide: #1 **Slides: #2 - #11** **Slide: #12**

✓ **^{32}Si:** A New Chronometer for Nuclear Dating

✓ **Application[1]:** Environmental sciences (dating 100 to 1000 years)

✓ **Artificially Produced:** Proton irradiation of metallic vanadium discs
(= *yielded world-wide unique amount; currently 20 MBq of ^{32}Si*)

✓ **Chemical Separation Process[2]:** Highly selective and robust

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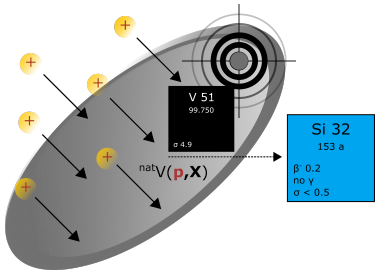
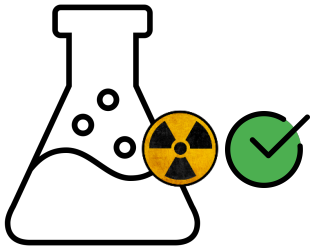
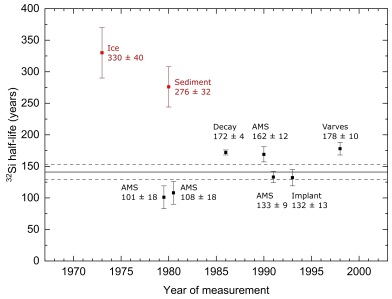
O **Half-life** determination ongoing (**various measurements**)







References

[1] Morgenstern, U., et al. (2001) *Radiocarbon*, **43**(2B), 909-916.

[2] Veicht, M., et al. (2021) *Radiochimica Acta*

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R&D Depart.

TRISKEM

Expertise in Separation Chemistry

Thank you!

FNSNF

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Fondo nazionale svizzero
Swiss National Science Foundation

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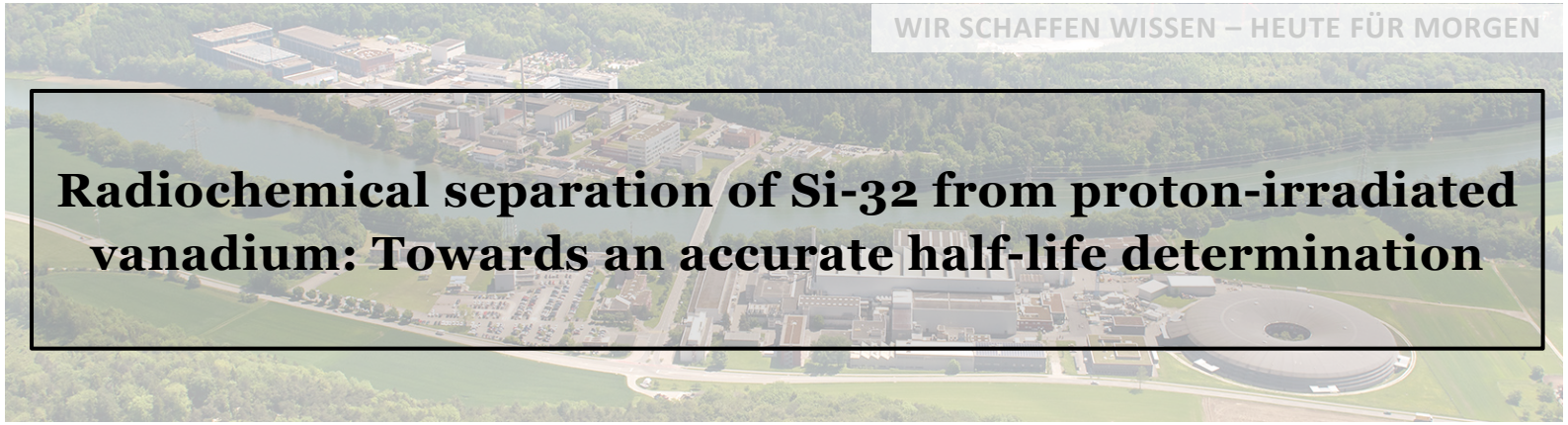

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