Automated quantification of 99-technetium in aqueous samples by means of online SPE-IC-ICP-MS

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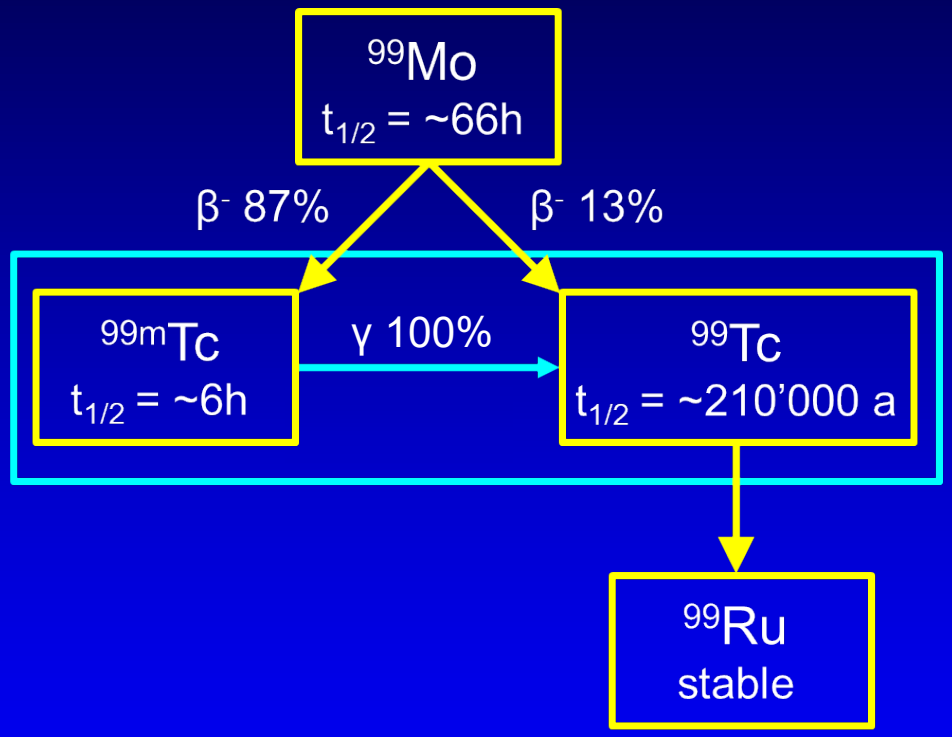
Technetium

- First artificial element reported (E. Segrè/C. Perrier, 1937)
- All known isotopes are radioactive → ^{99}Tc most common
  - β^- decay with a half life of ~210,000 years
  - Natural occurrence negligible
- Virtually monoisotopic with ^{99}Tc mainly from anthropogenic sources
  - Nuclear weapons testing, reactors and reprocessing plants
  - Examples: Hanford (US), La Hague (FR), Sellafield (GB)

Technetium

- Metastable ^{99m}Tc used in medical diagnosis
- γ-emitter with a half life of ~6 hours
  - Tracer in scintigraphic techniques
  - Method to visualize metabolic activity in target tissues
- Provided by "technetium-99m generators" on-site in local hospitals
  - MoO_4^{2-} used as a source for ^{99m}Tc



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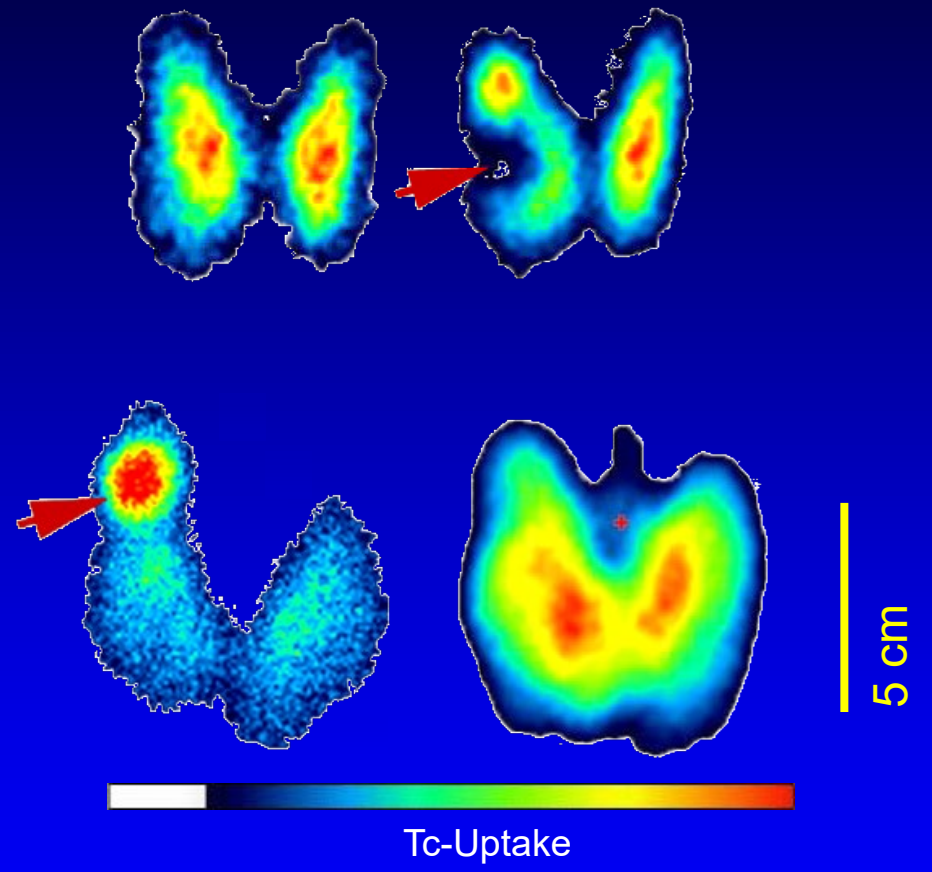

Scintigraphic image of a thyroid gland

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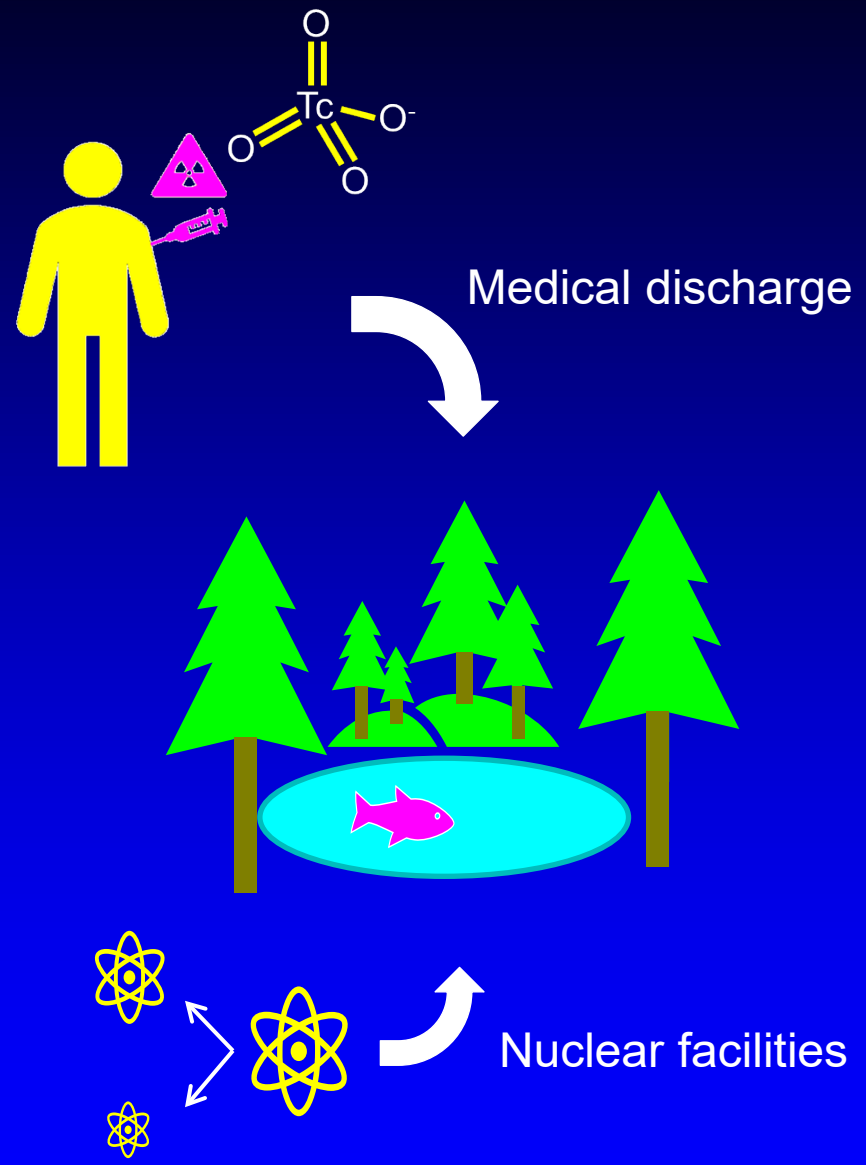

Method Development – Tc Quantification using ICP-MS

- Sensitive quantification of ^{99}Tc using inductively coupled plasma mass spectrometry

Apex Q
High sensitivity
sample introduction system

Agilent 7700-SQ-ICP-MS

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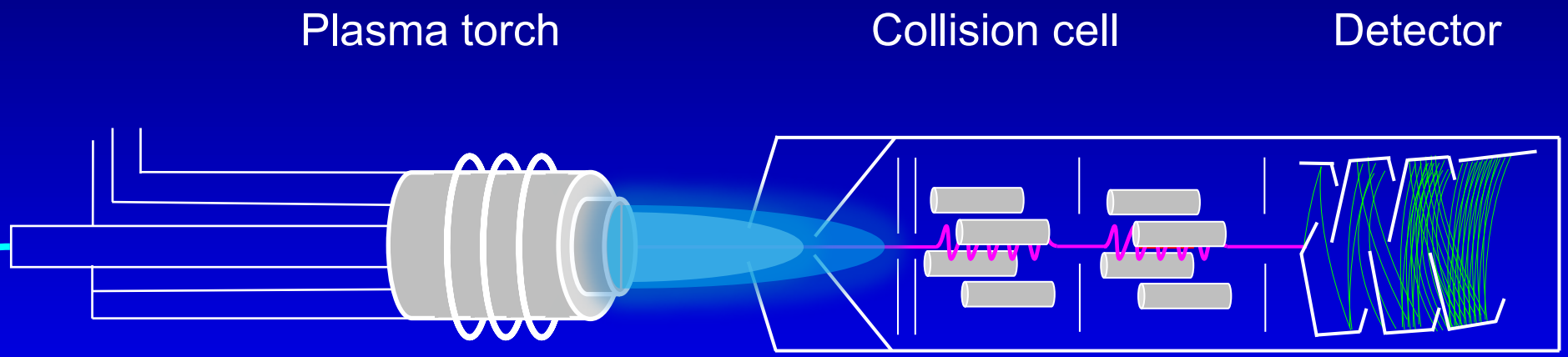
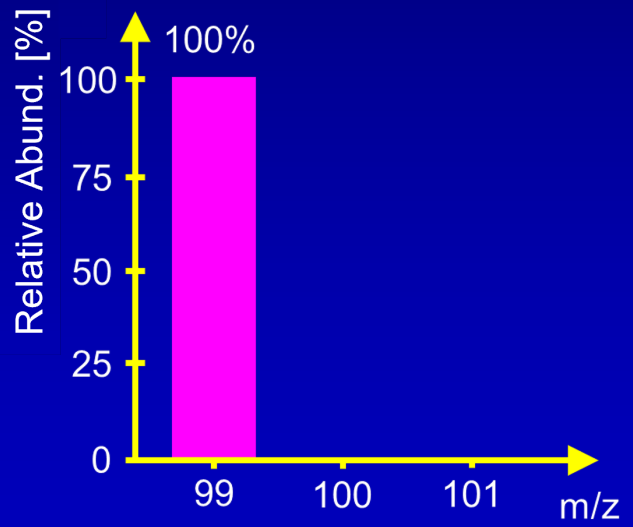


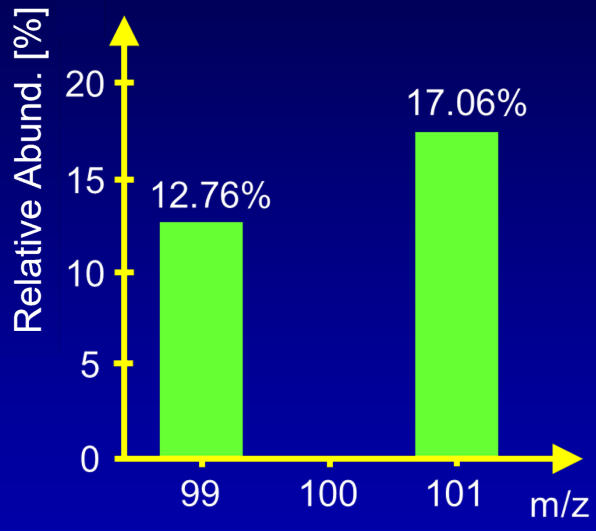
Quantification strategy for ICP-MS – isobaric dilution analysis

- Tc virtually monoisotopic
- Standards not easily available
- Internal standard favorable

Sample with y µg/L ^{99}Tc



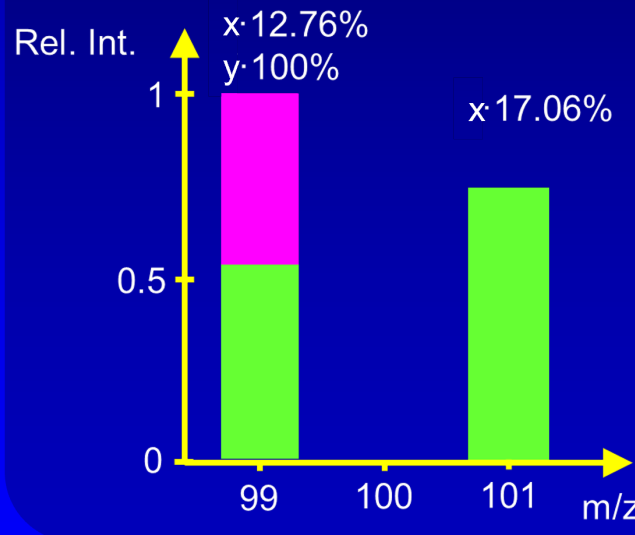
x µg/L Ru with natural isotope ratio



Spiking with Ru

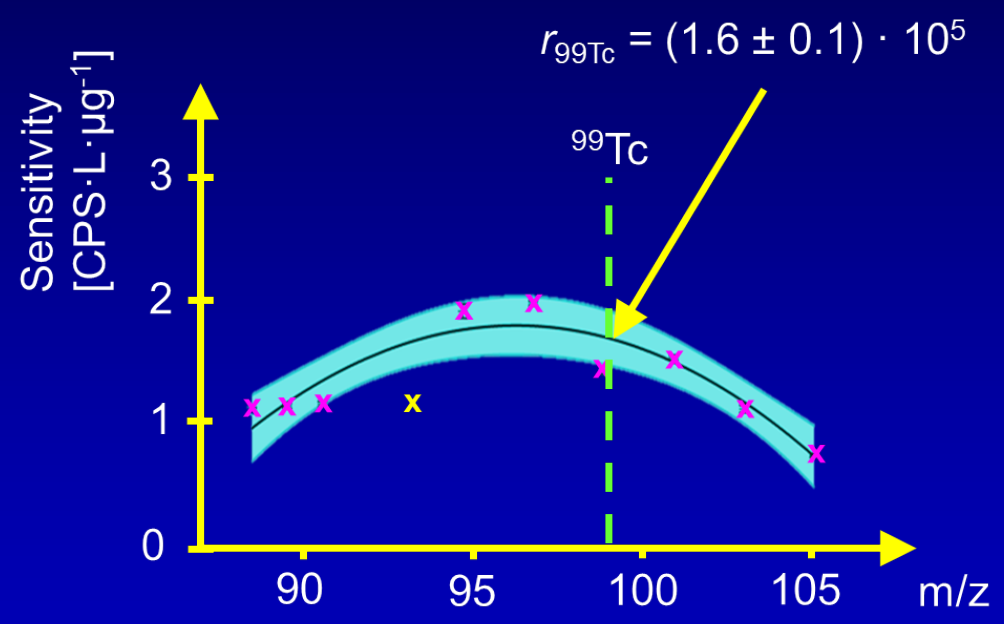
- Specific sensitivity
- Mass bias correction

Spiked sample with Ru and ^{99}Tc



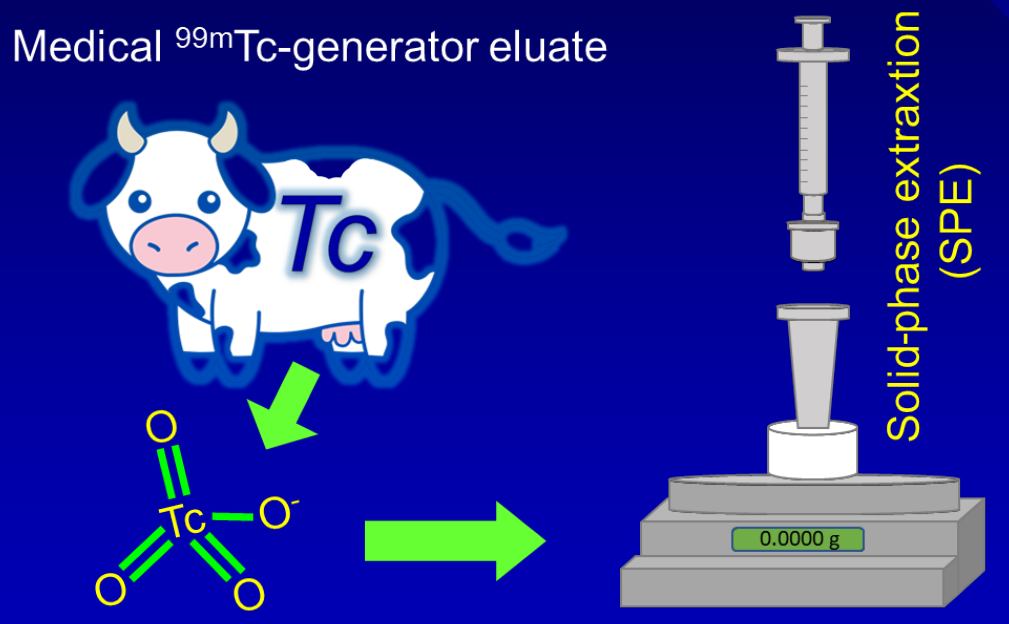
Isobaric dilution analysis – ICP-MS sensitivity correction

- Different specific elemental responses of Tc and Ru need to be recognized



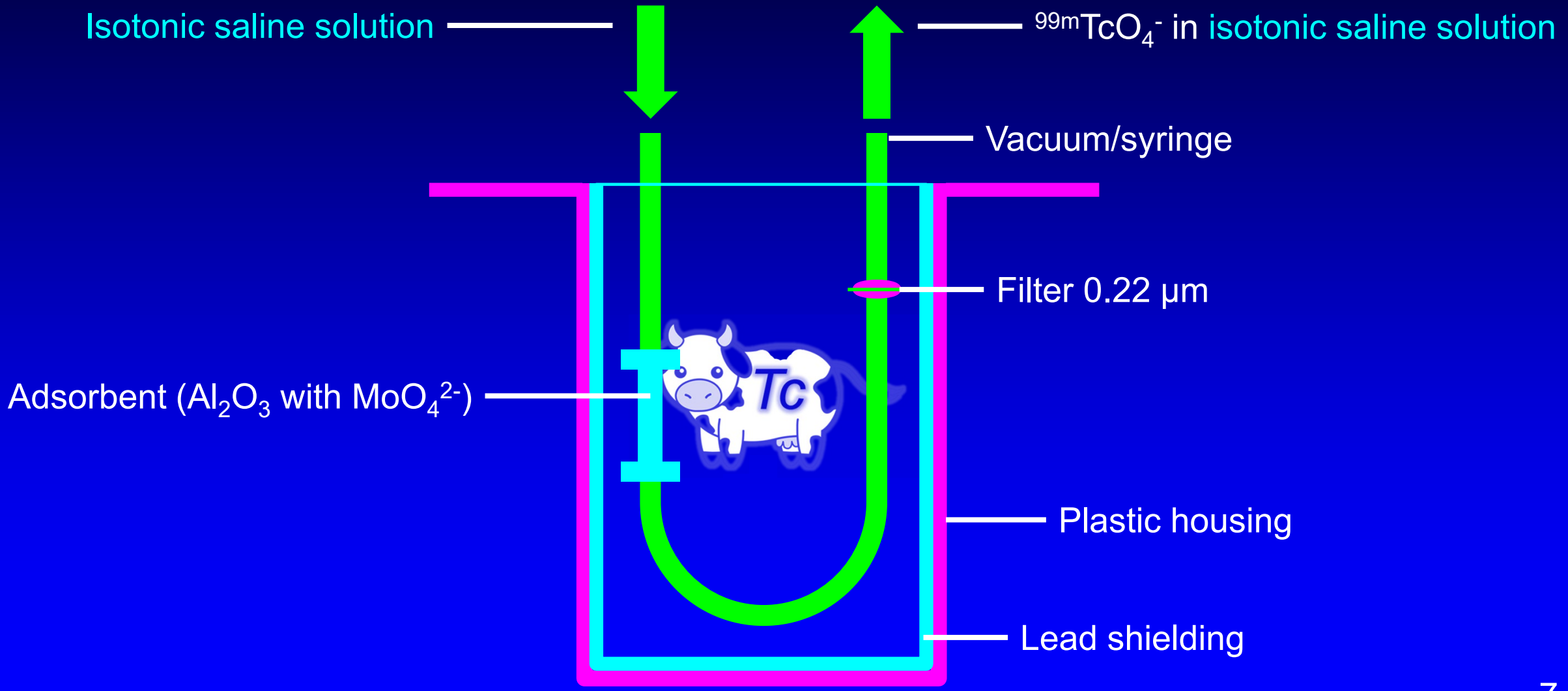
→ Higher uncertainty of ~10%

vs.



→ Direct sensitivity determination

Technetium-99m generator



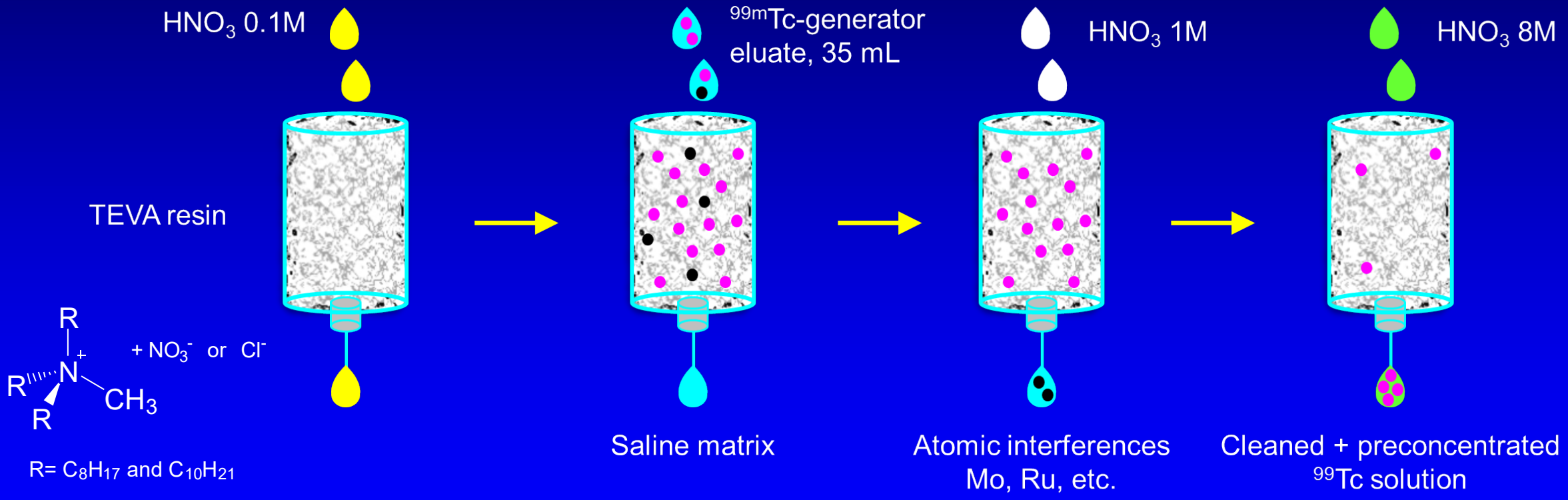
Generation of a ^{99}Tc-Standard – solid phase extraction (SPE)

Steps: 1) Conditioning

R= C_8H_{17} and $C_{10}H_{21}$

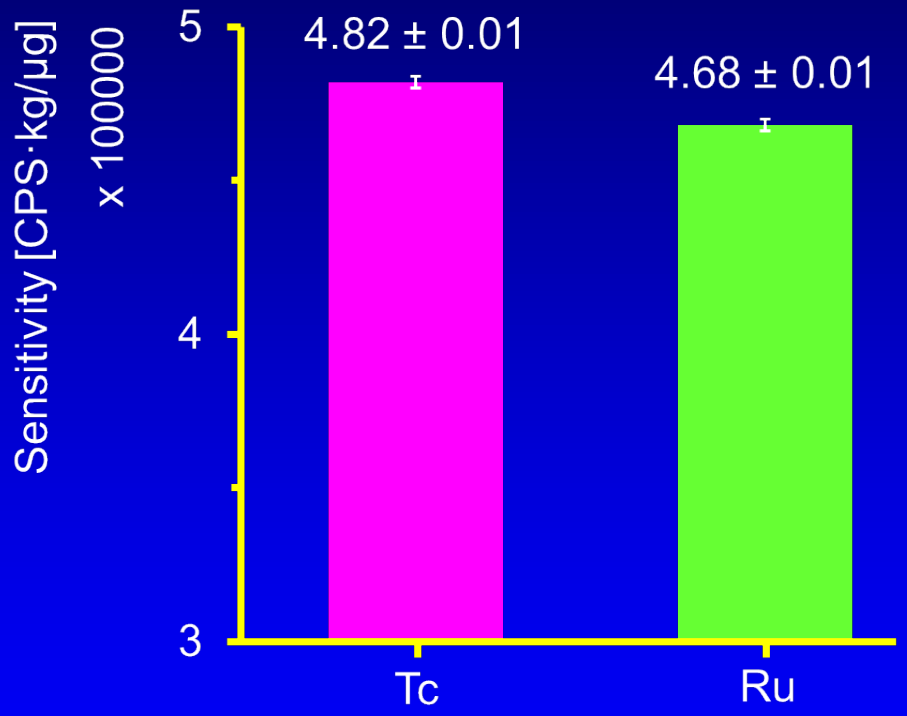
Generation of a ^{99}Tc-Standard – solid phase extraction (SPE)

Steps: 1) Conditioning 2) Loading 3) Washing 4) Eluting

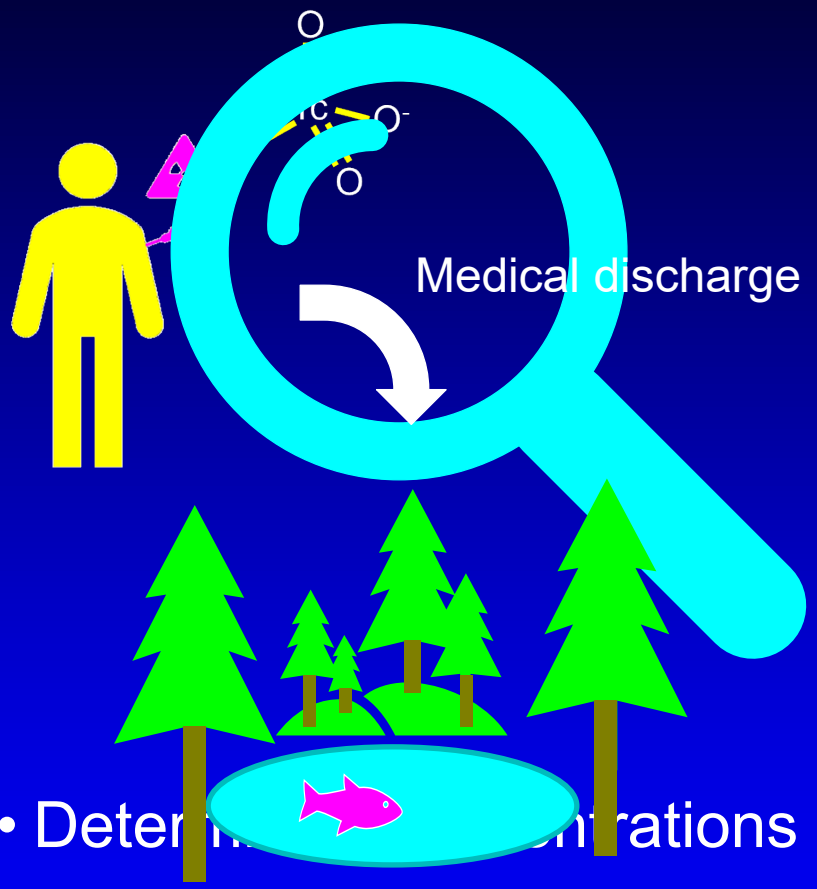


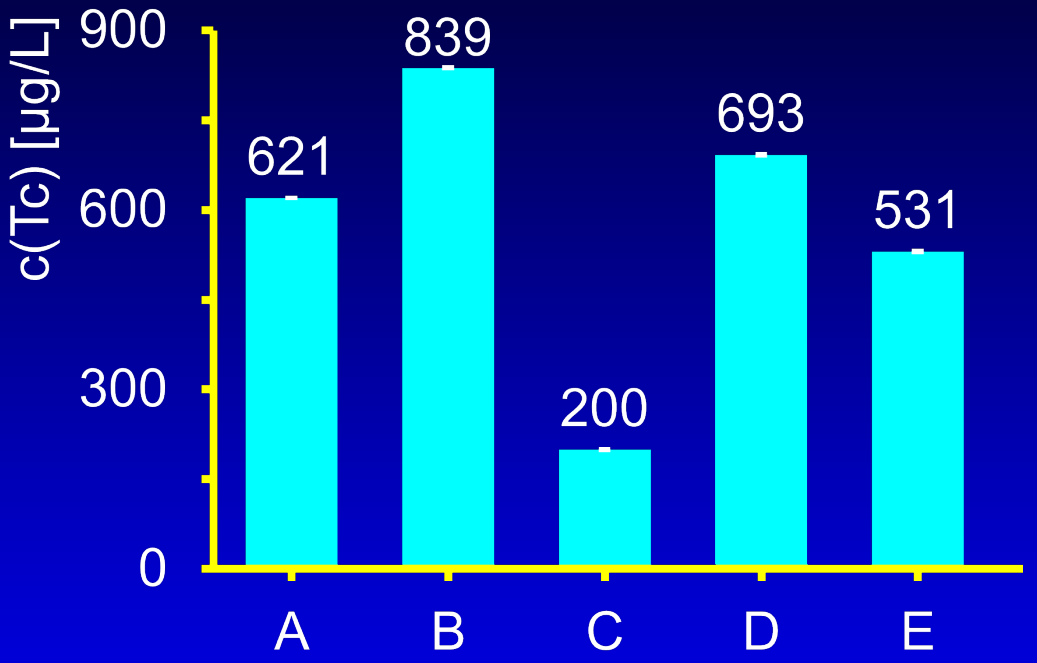
Generation of a ^{99}Tc-standard – solid phase extraction (SPE)

- Quantifying ^{99}Tc standard using X-ray fluorescence analysis (XRF)
- Direct sensitivity determination of Tc
- Sensitivity differences of Tc and Ru
  - Better ionization and transfer of Tc
  - Correction of sensitivity differences possible within the equation of IBDA

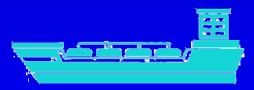


Application in offline IBDA – Tc-generator eluate

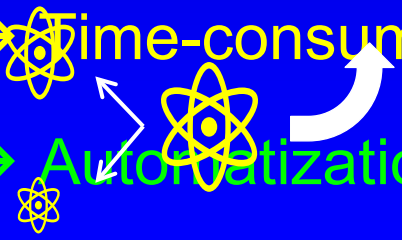




- Determination of concentrations between (200 ± 1) µg/L and (839 ± 1) µg/L



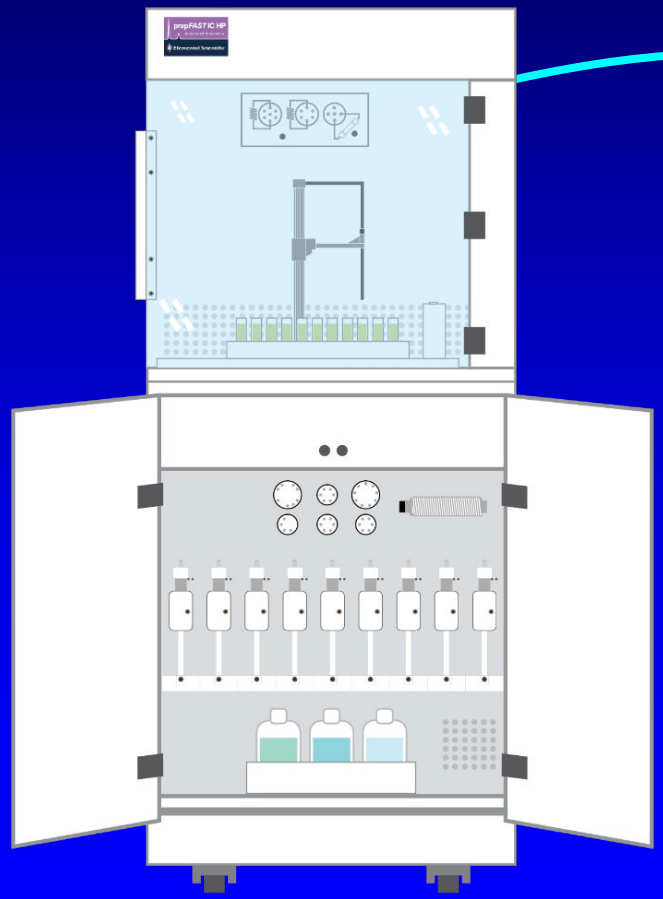
→ Time-consuming and limited to higher concentrations



→ Automatization and preconcentration

Application in automated online IBDA

- Automated single platform system for total and speciation analysis (prep*Fast* IC)



prep*Fast* IC-System

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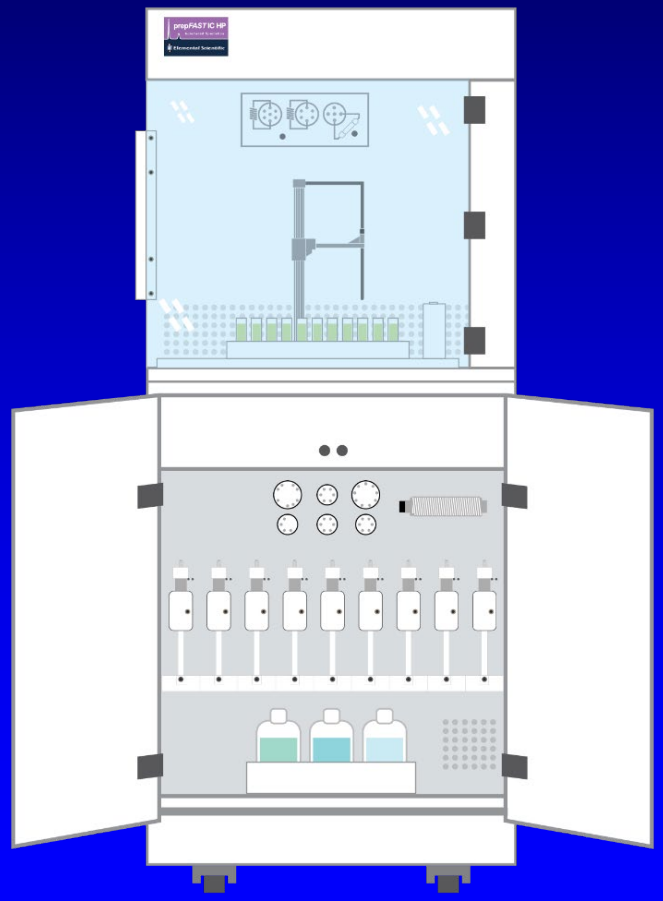

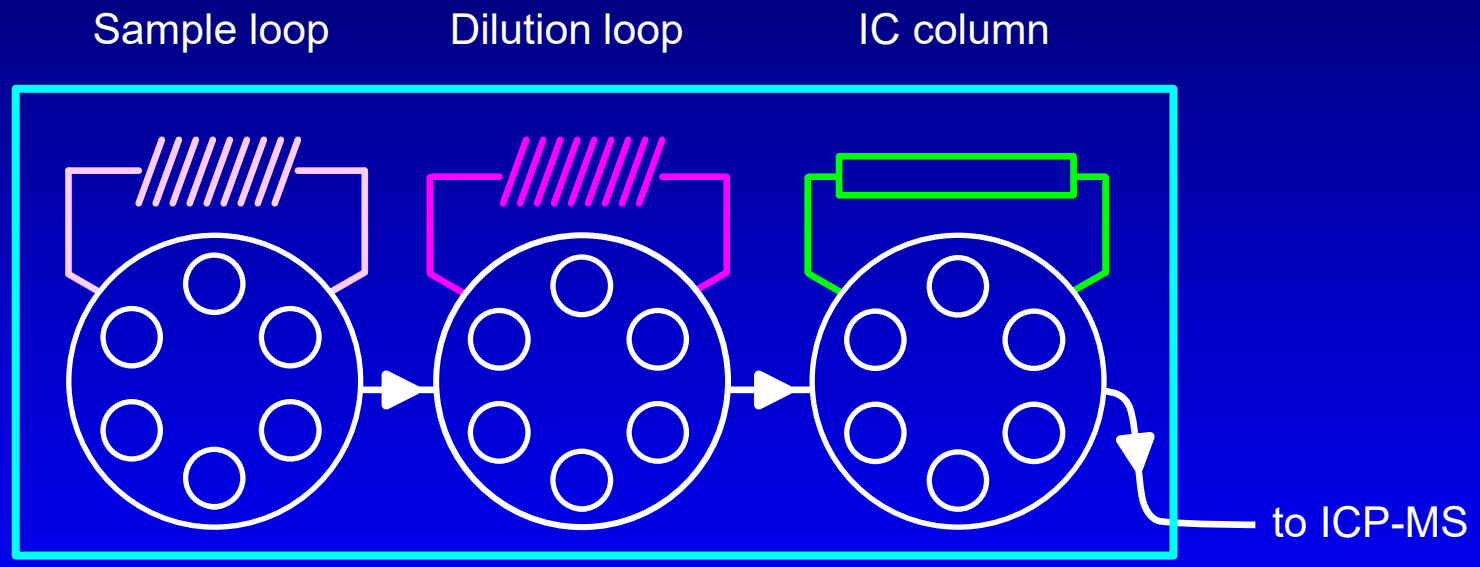

- Syringe-driven: automated dilution of standards and samples
- External and internal calibration possible

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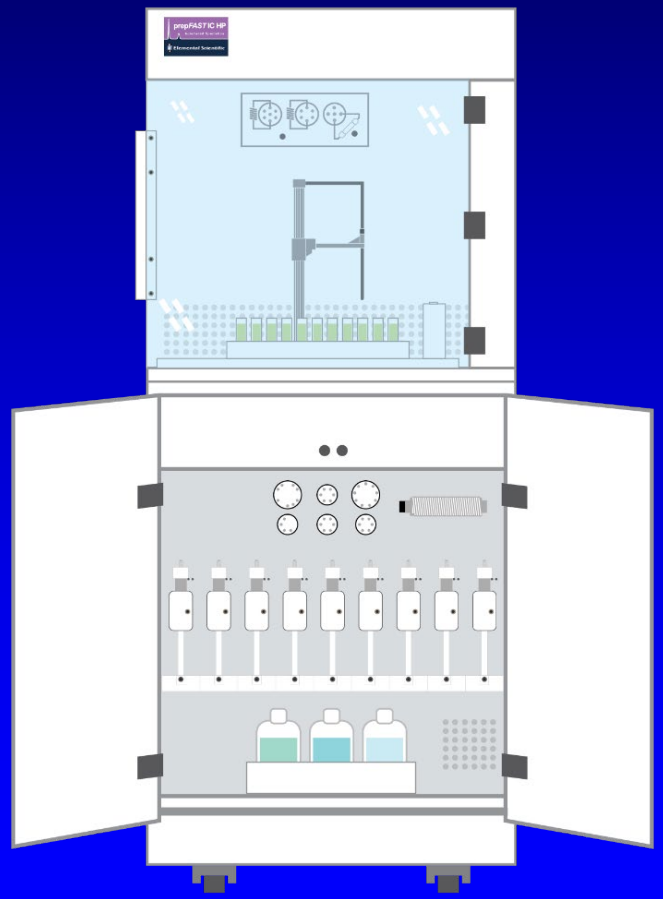
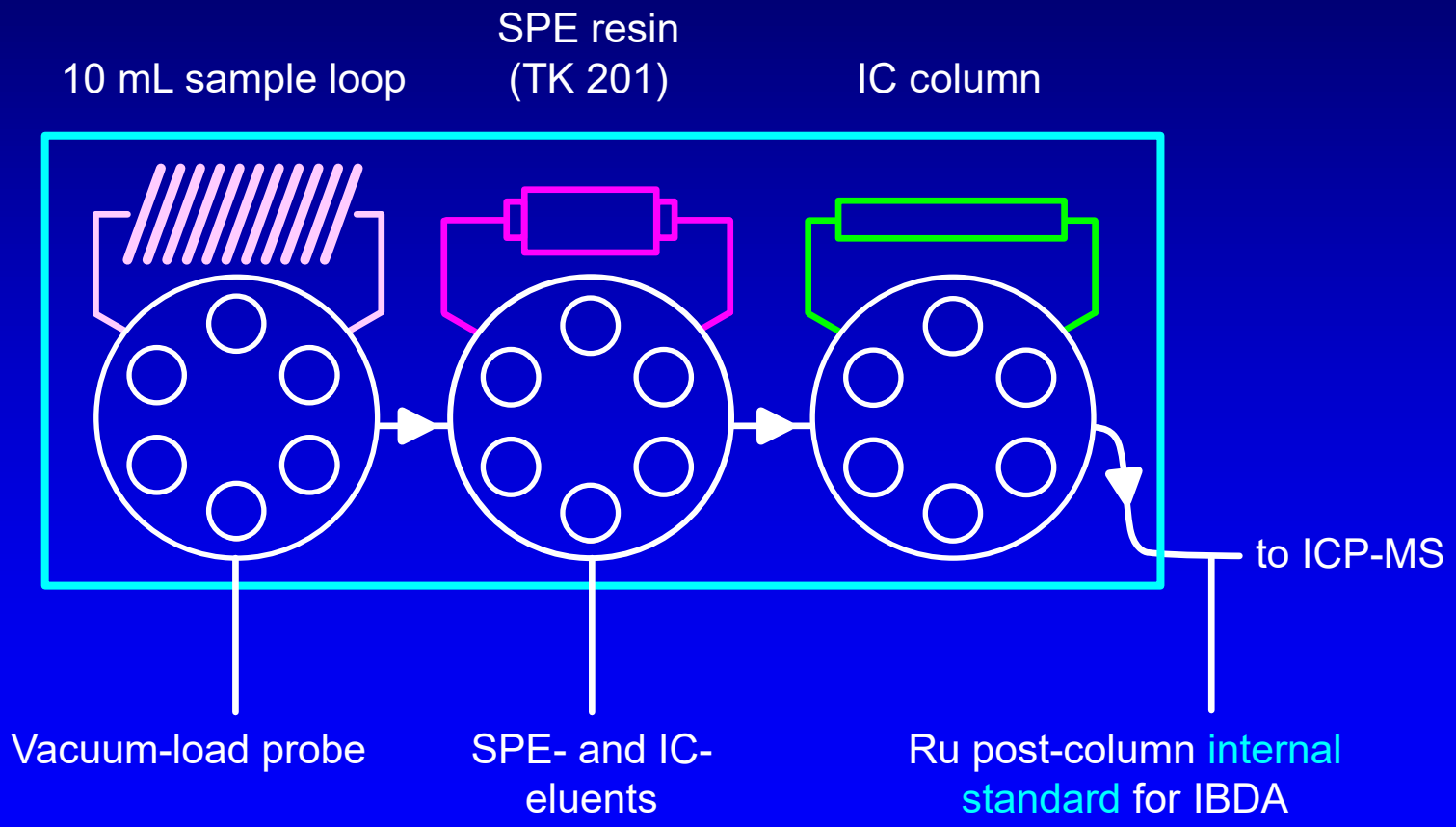
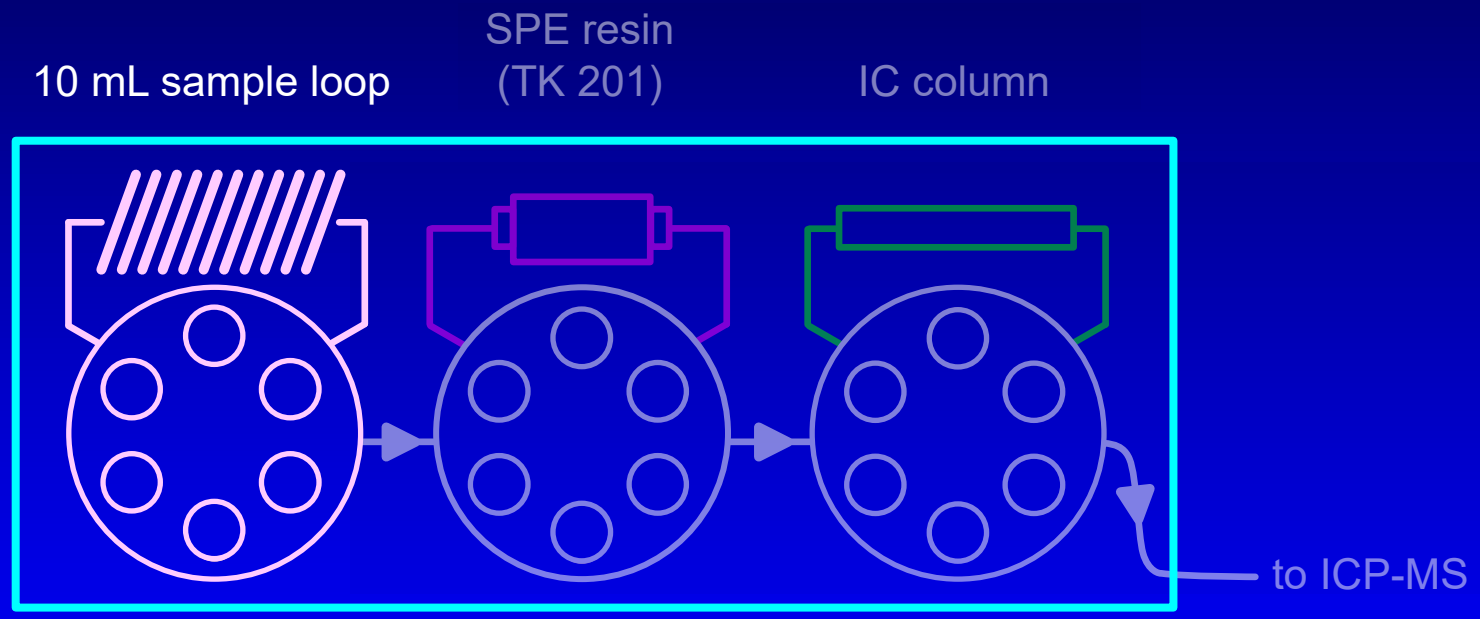




Application in automated online IBDA

- Automated online SPE - IC separation of ^{99}Tc with internal quantification using IBDA

1) Vacuum-load loop



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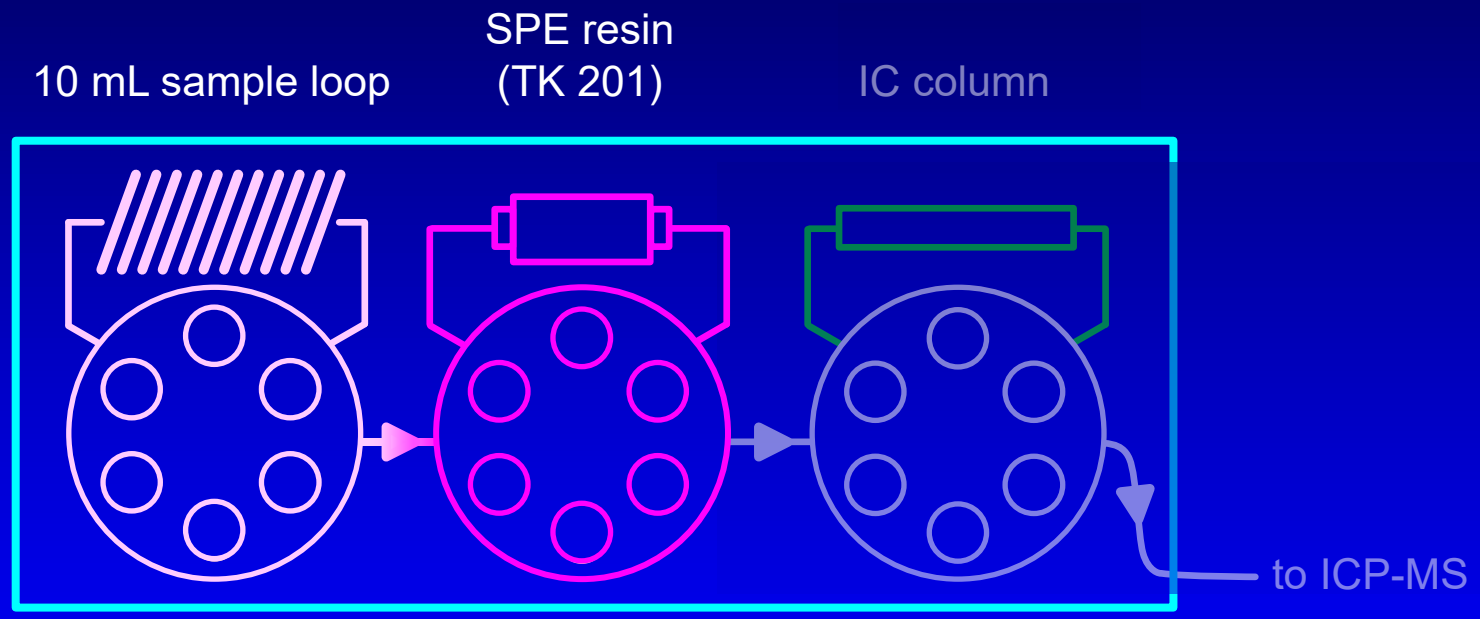
1) Vacuum-load loop

2) Load SPE cartridge (10 x 10 mL)



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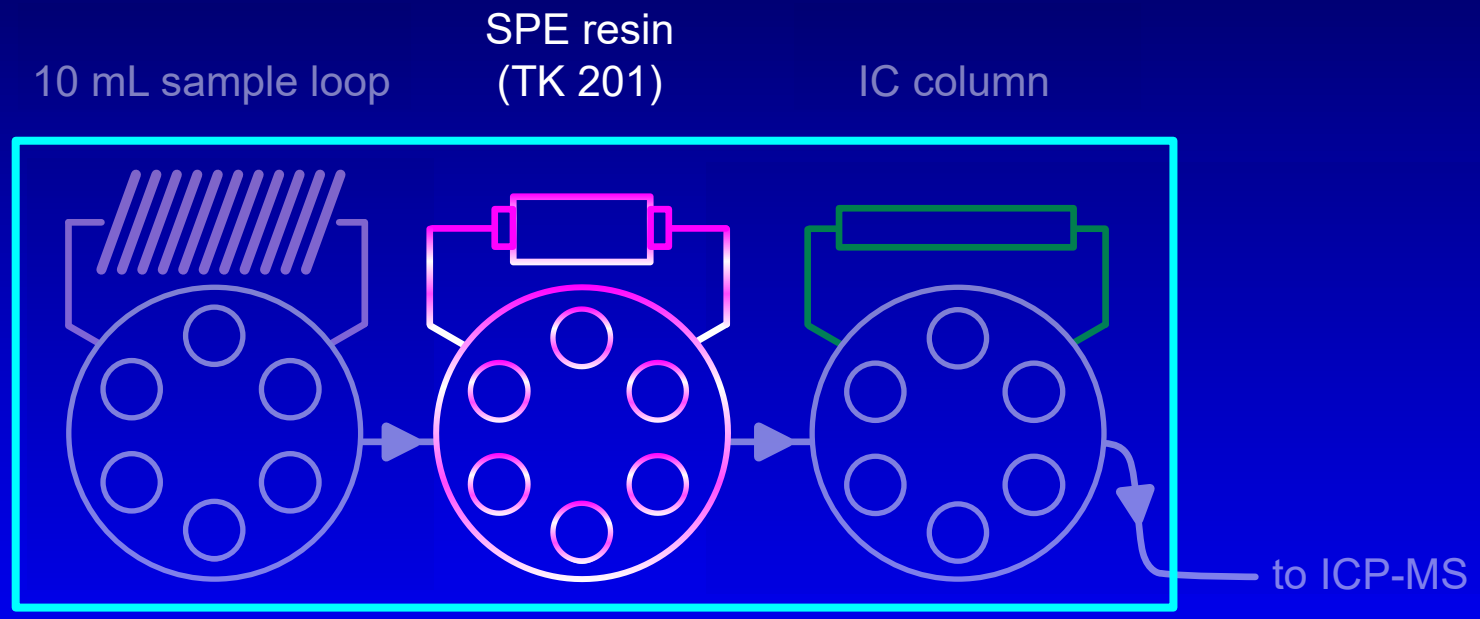
3) Wash SPE cartridge (0.01 M HNO_3)



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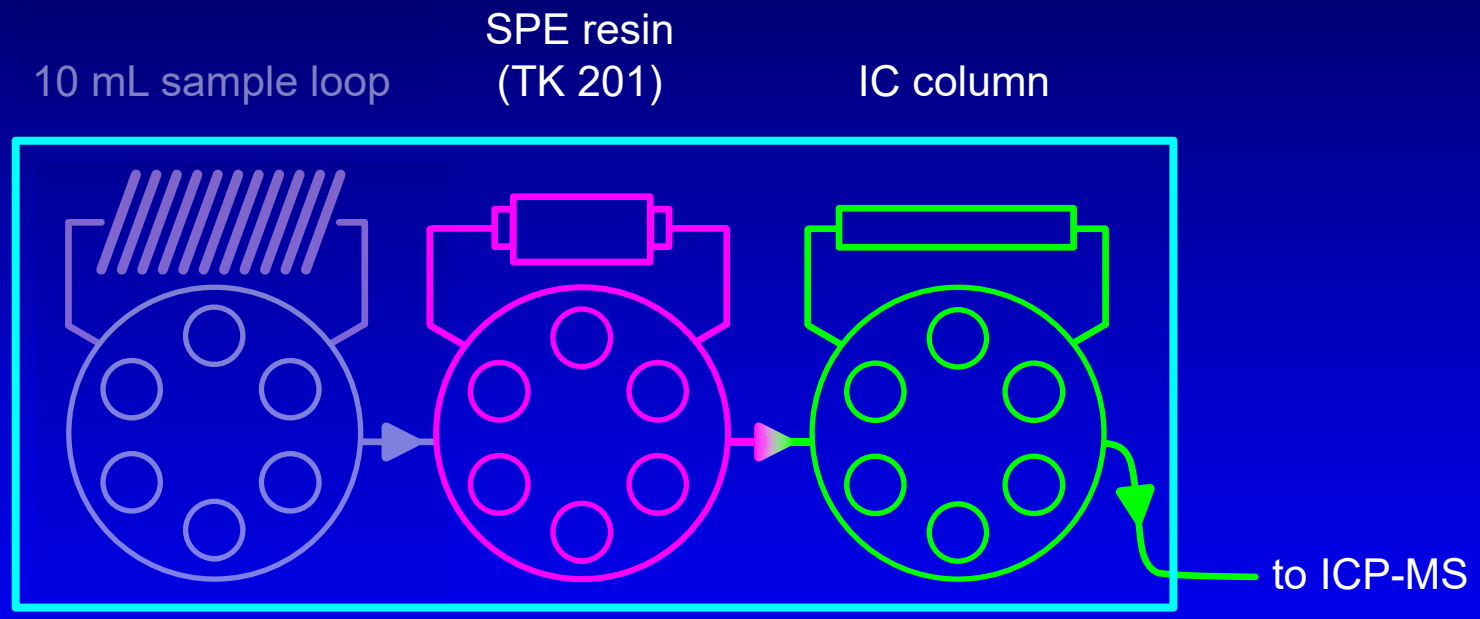
4) Elution gradient (SPE + IC column)

- SPE cartridge onto IC column (0.5 M NH_4OH)
- IC column (0.15 M NH_4NO_3)



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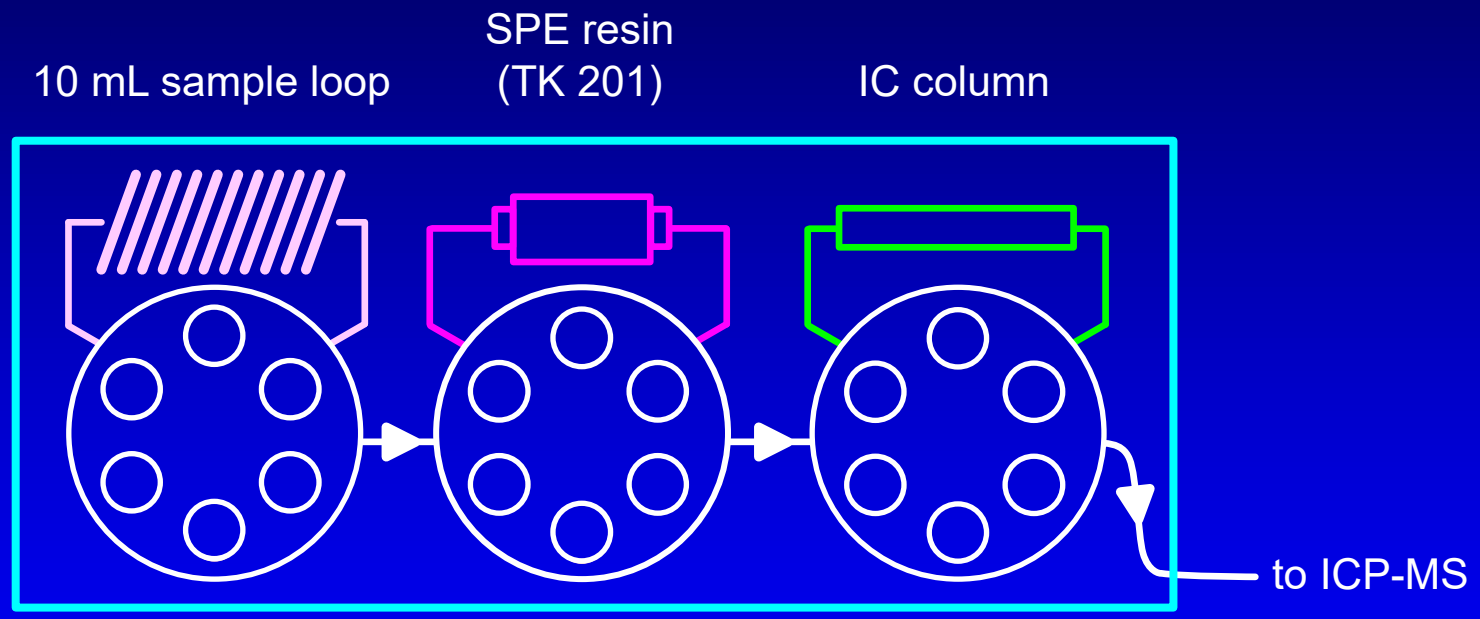
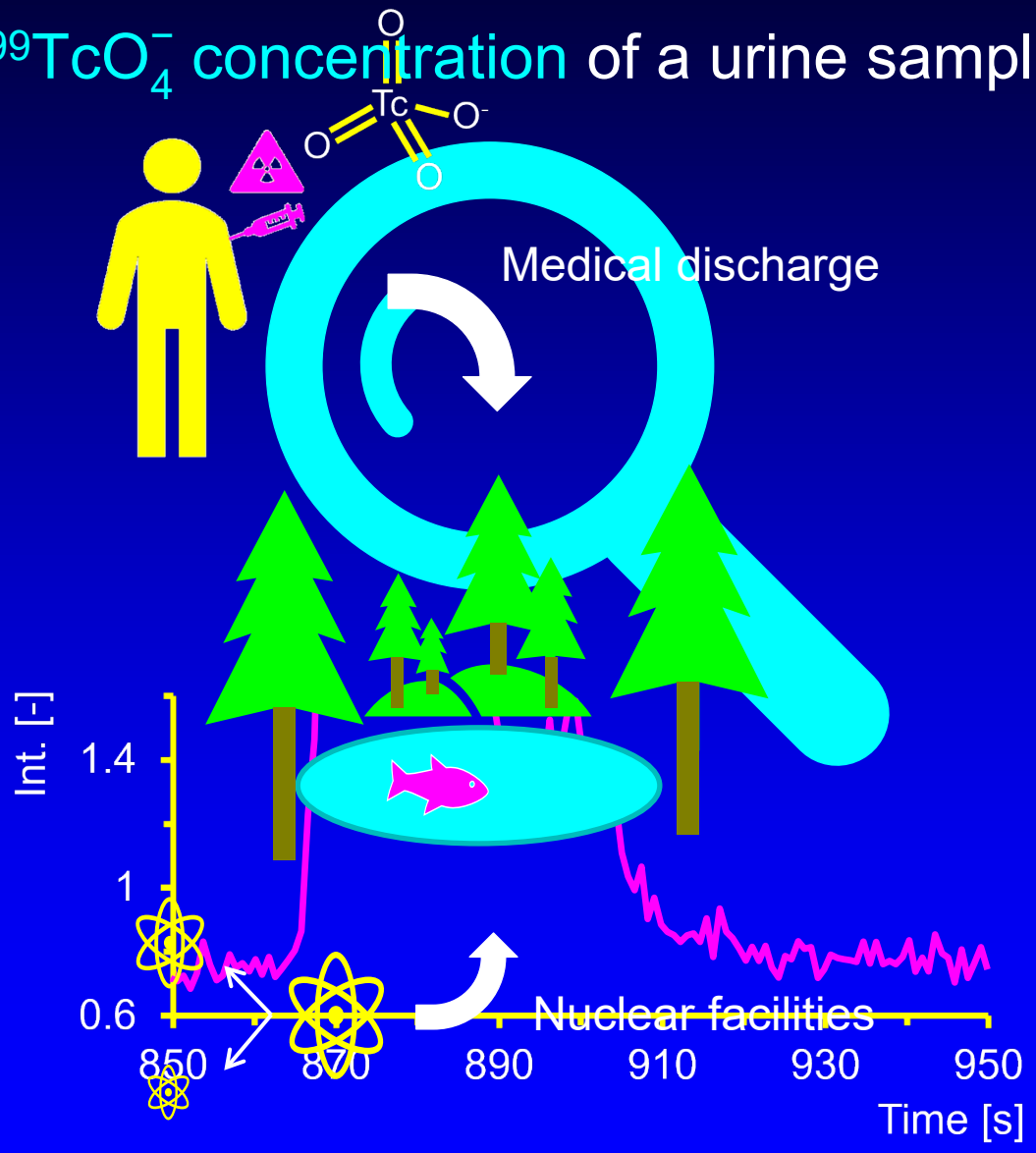
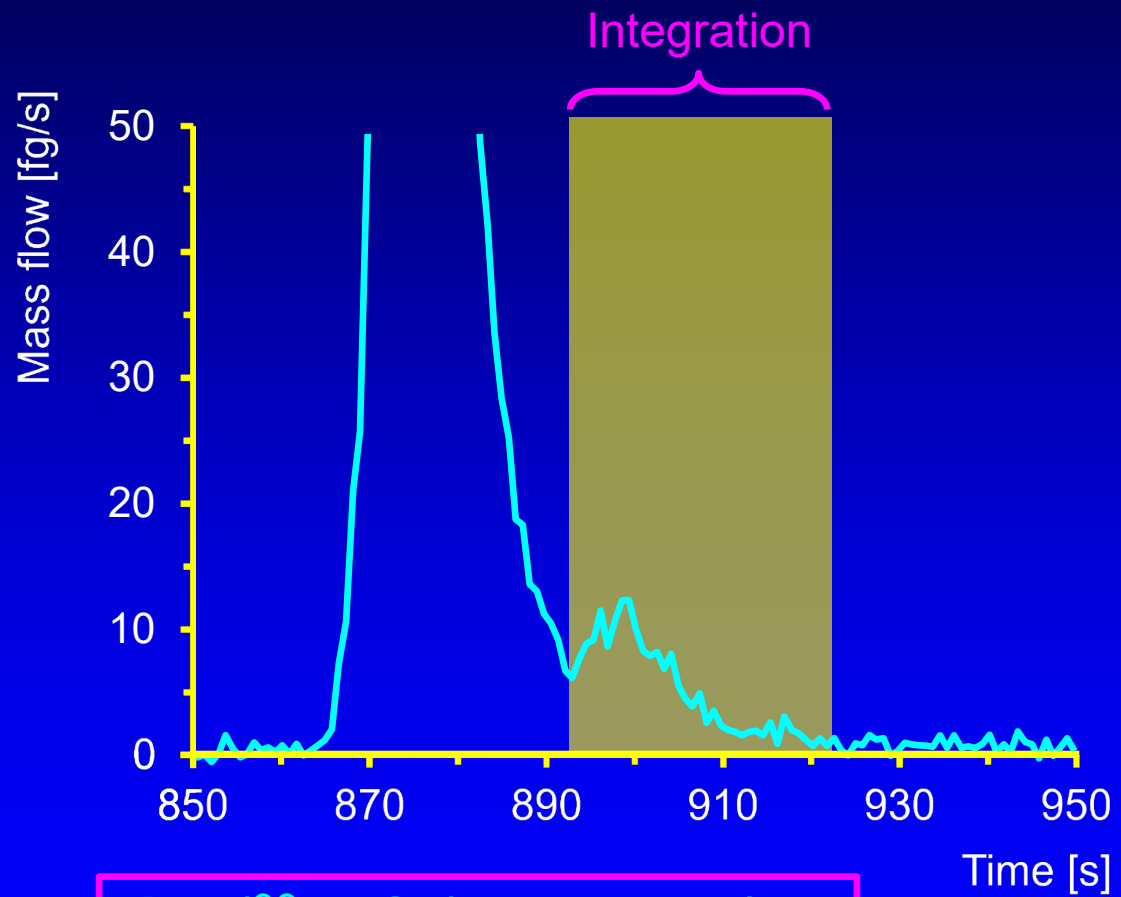


Application in automated online IBDA

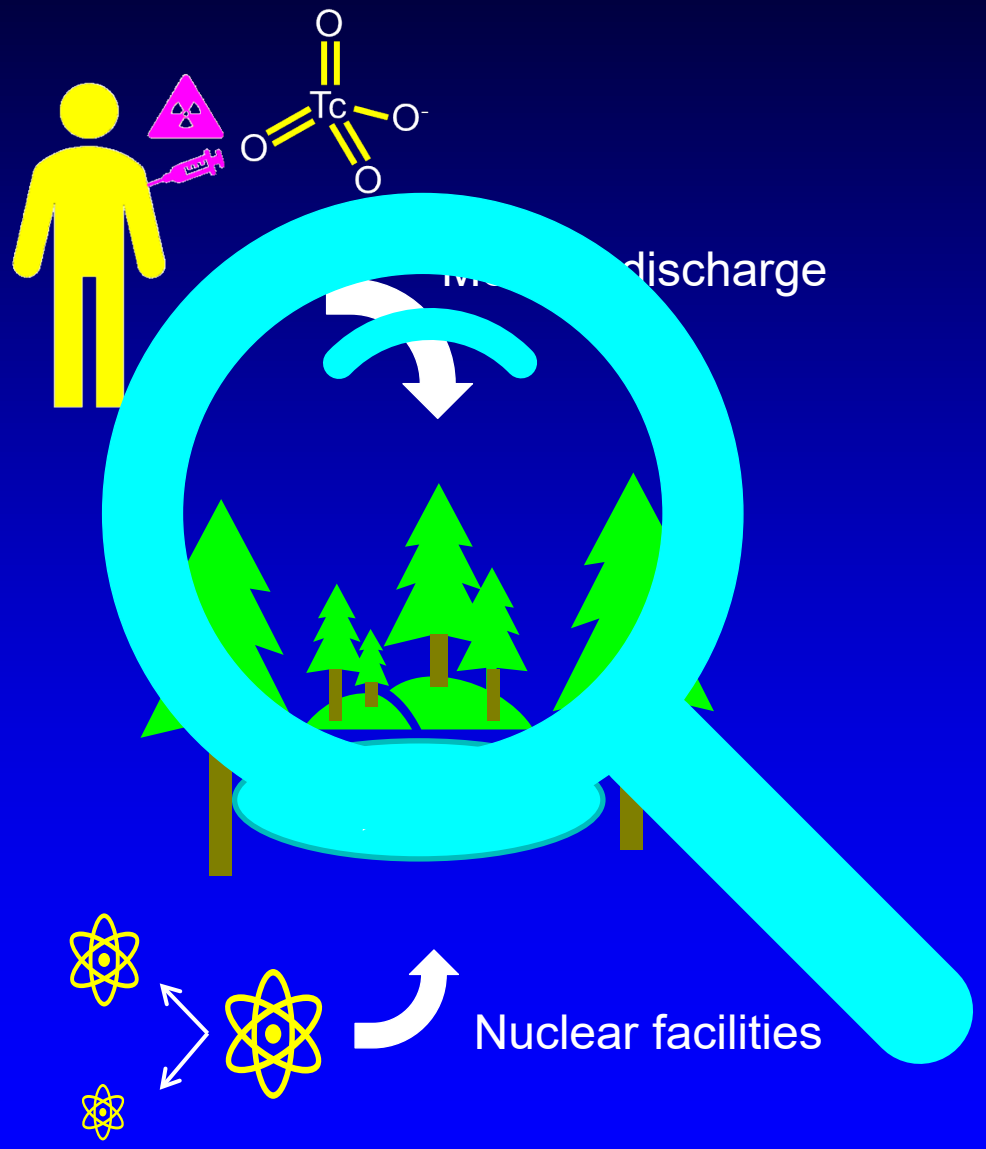
- $^{99}TcO_4^-$ concentration of a urine sample from a patient receiving bone scintigraphy





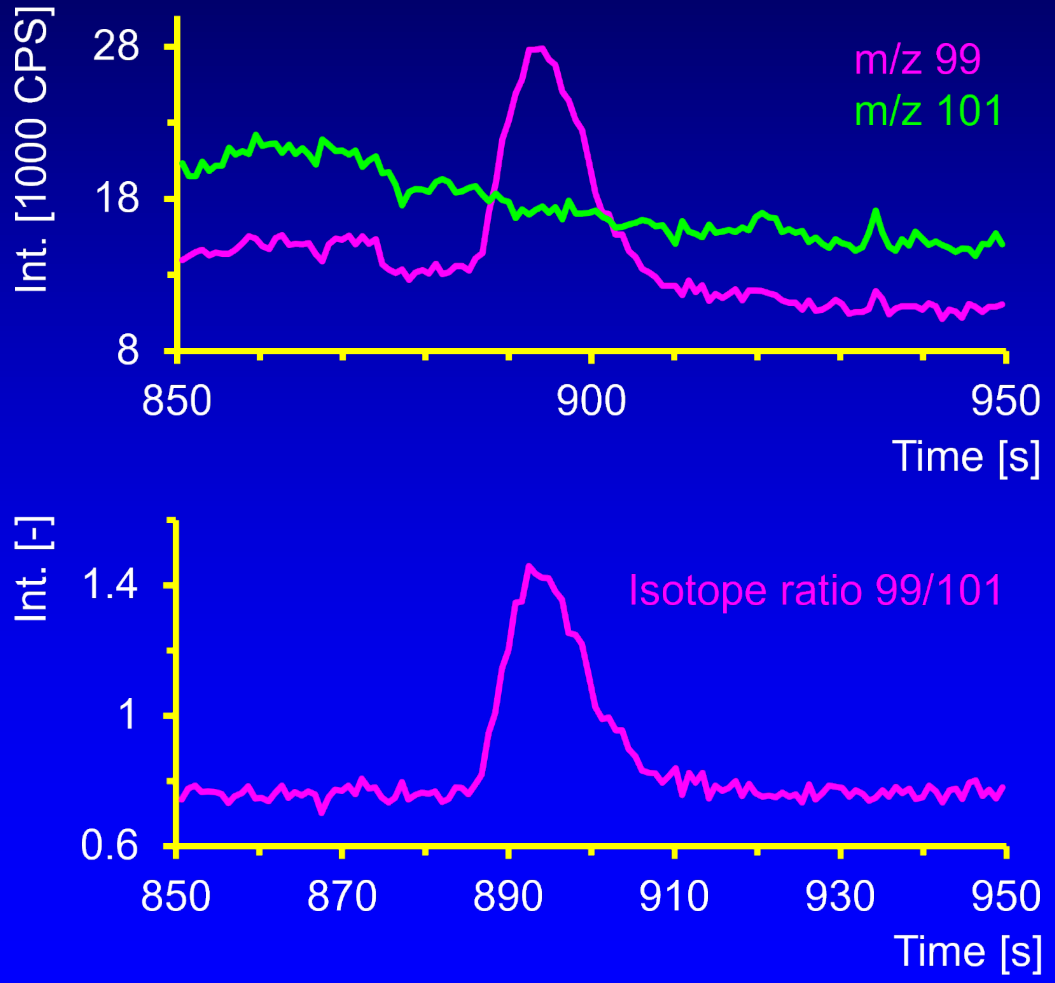
→ c($^{99}TcO_4^-$) = 2.5 ng/kg

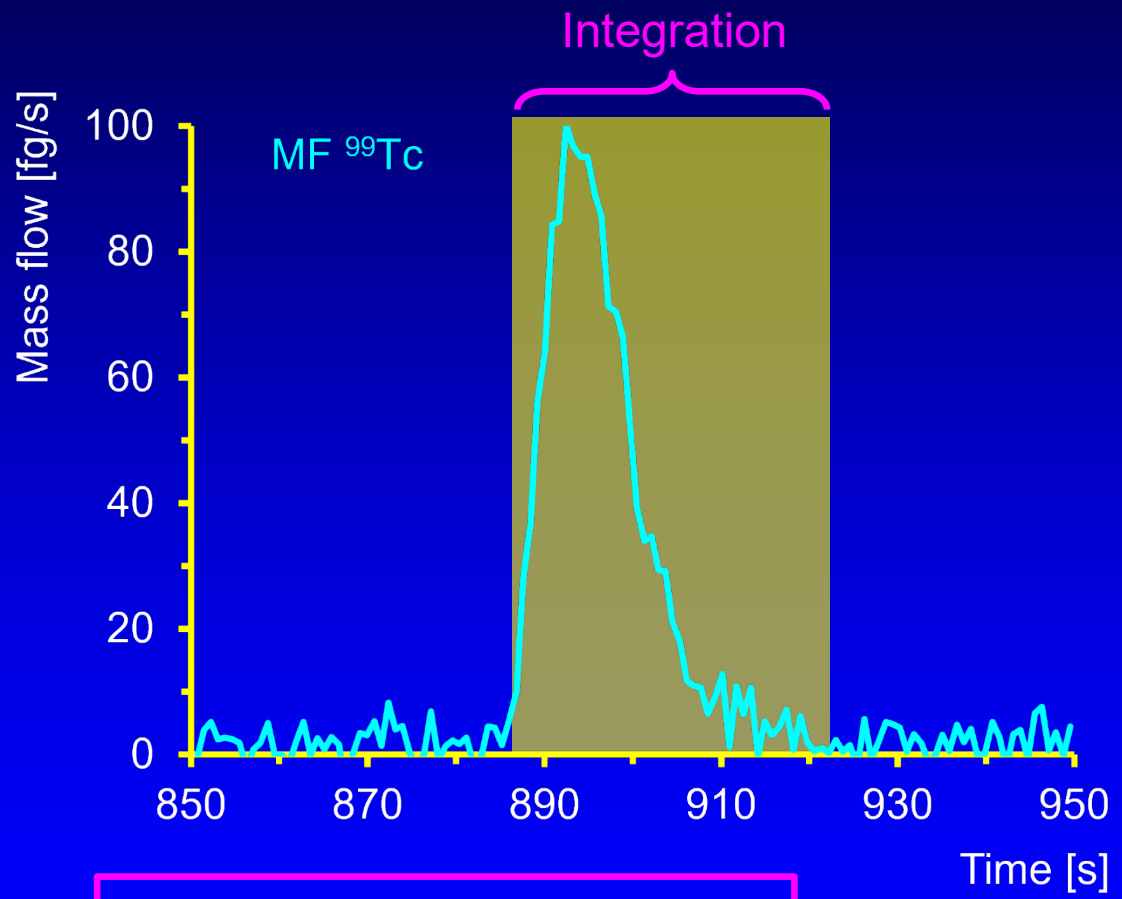
Application in automated online IBDA



Application in automated online IBDA

- Online SPE - IC separation of a spiked aqueous sample with c(Tc) = 10 pg/kg

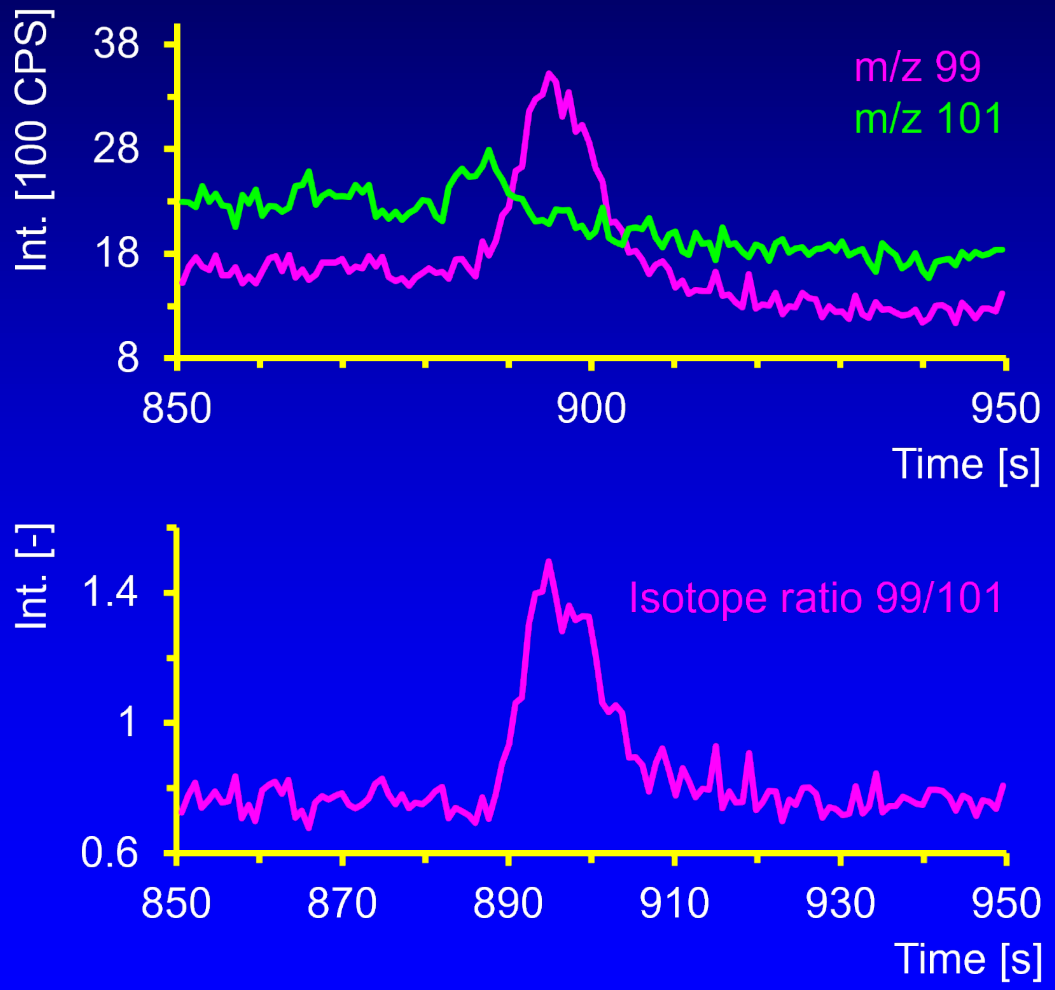


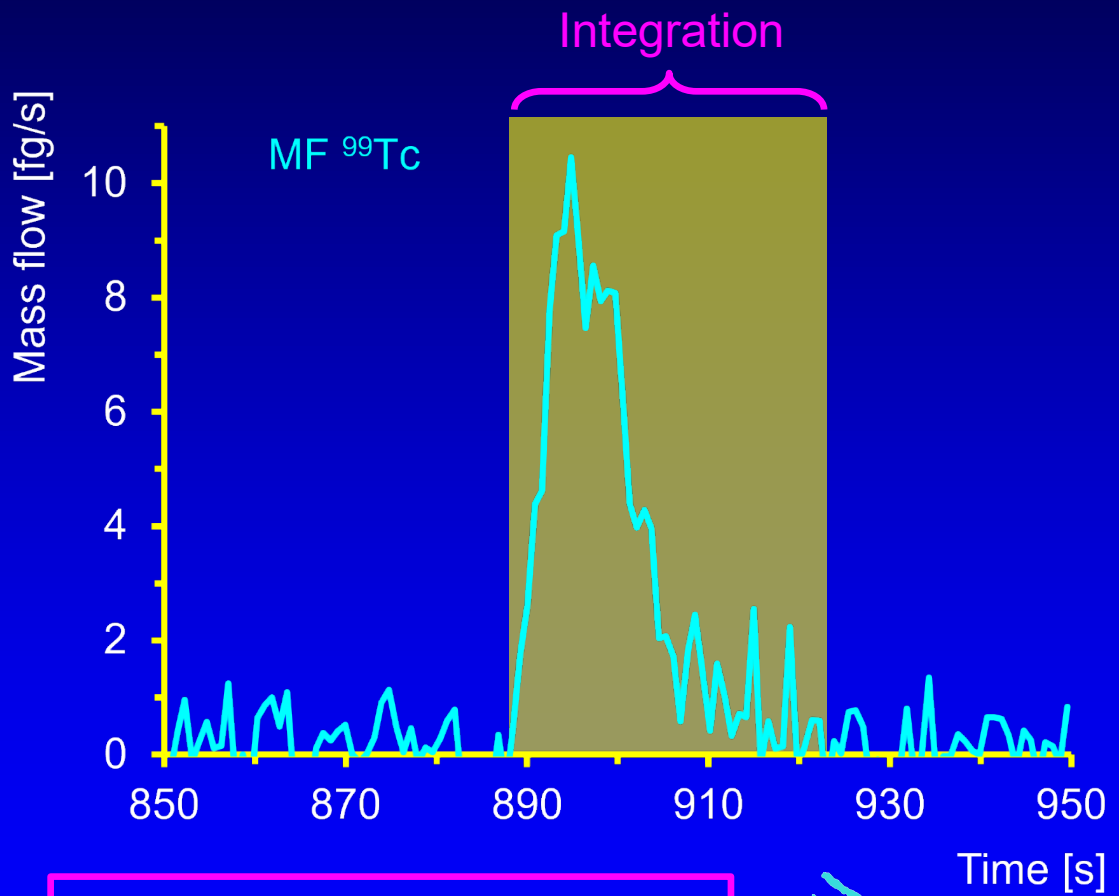


→ Recovery: 101±1 %

Application in automated online IBDA

- Online SPE - IC separation of a spiked aqueous sample with c(Tc) = 1 pg/kg

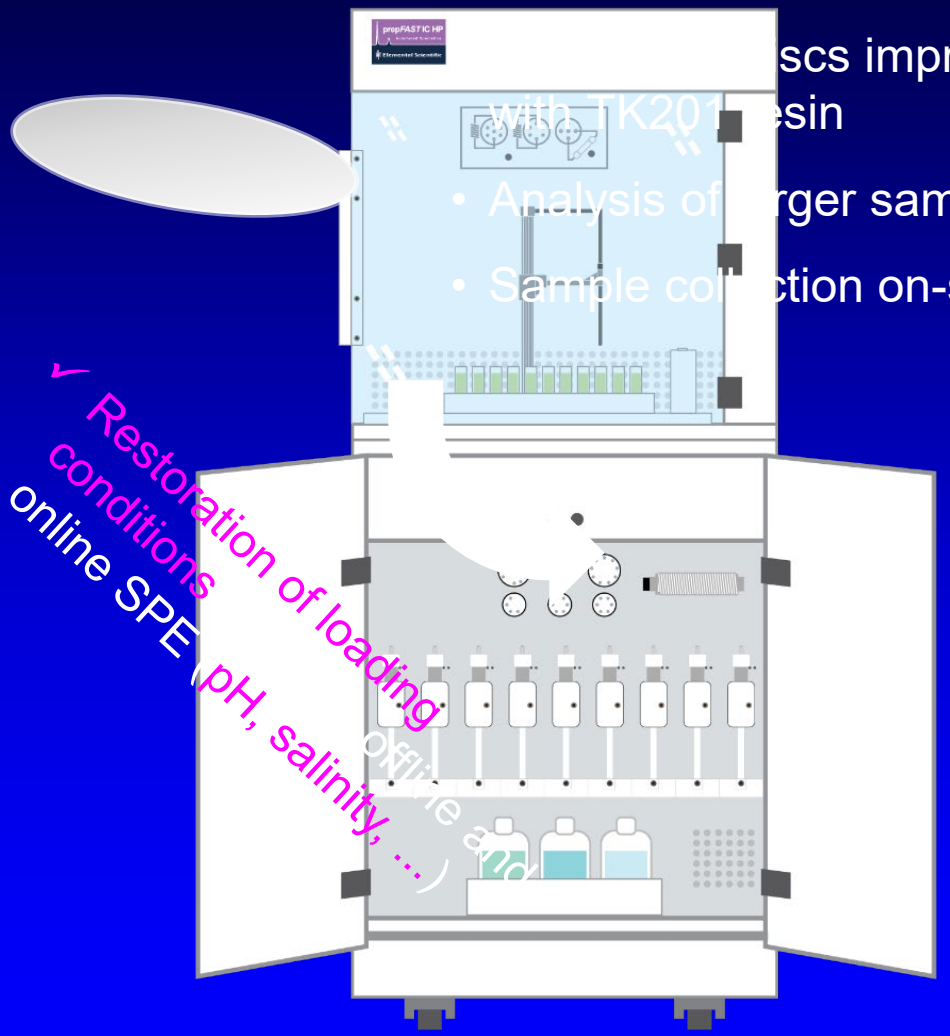




→ Recovery: 100±1 %

Latest Approach – Coupling of online and offline SPE

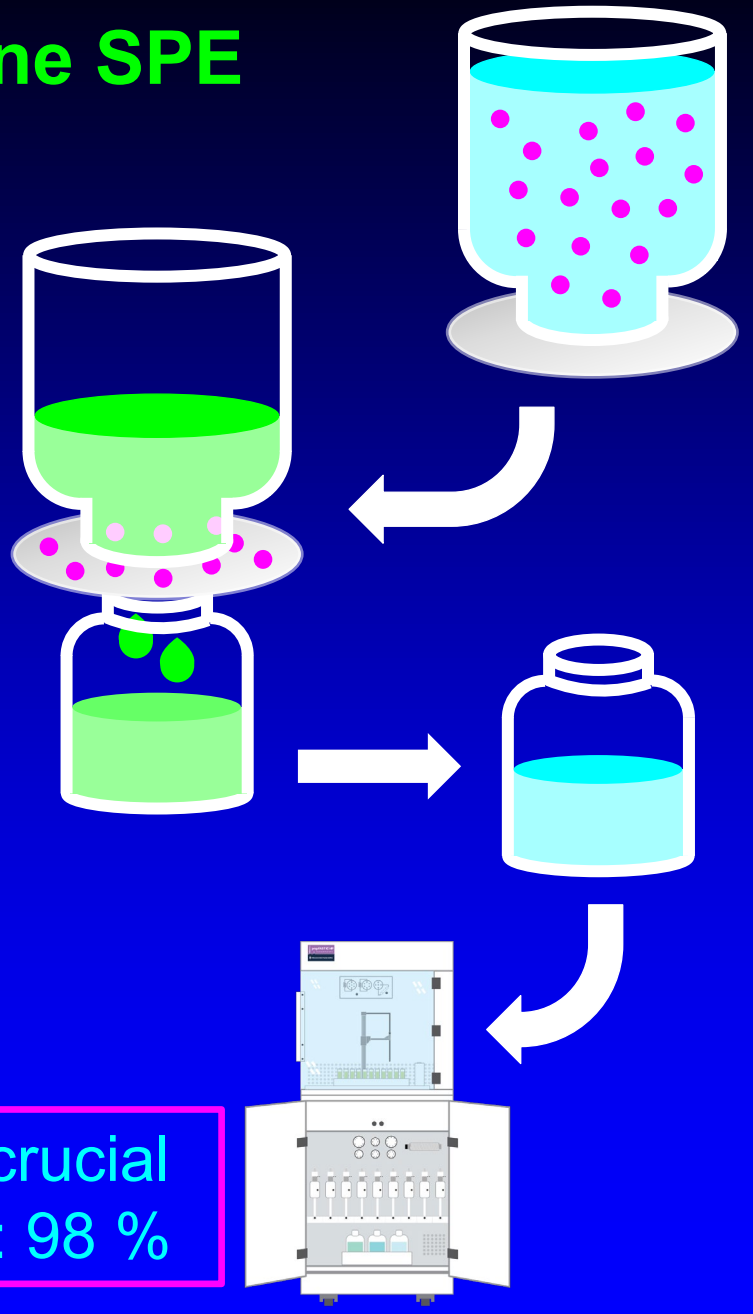
- Online SPE - Method works with volumes up to ~100 mL
- Some samples require even lower detection limits
  - Higher grade of preconcentration
- Some samples demand on-site handling
  - Safety requirements, large sample volumes, ...



Coupling of online and offline SPE

Experimental workflow: Offline + Online SPE:

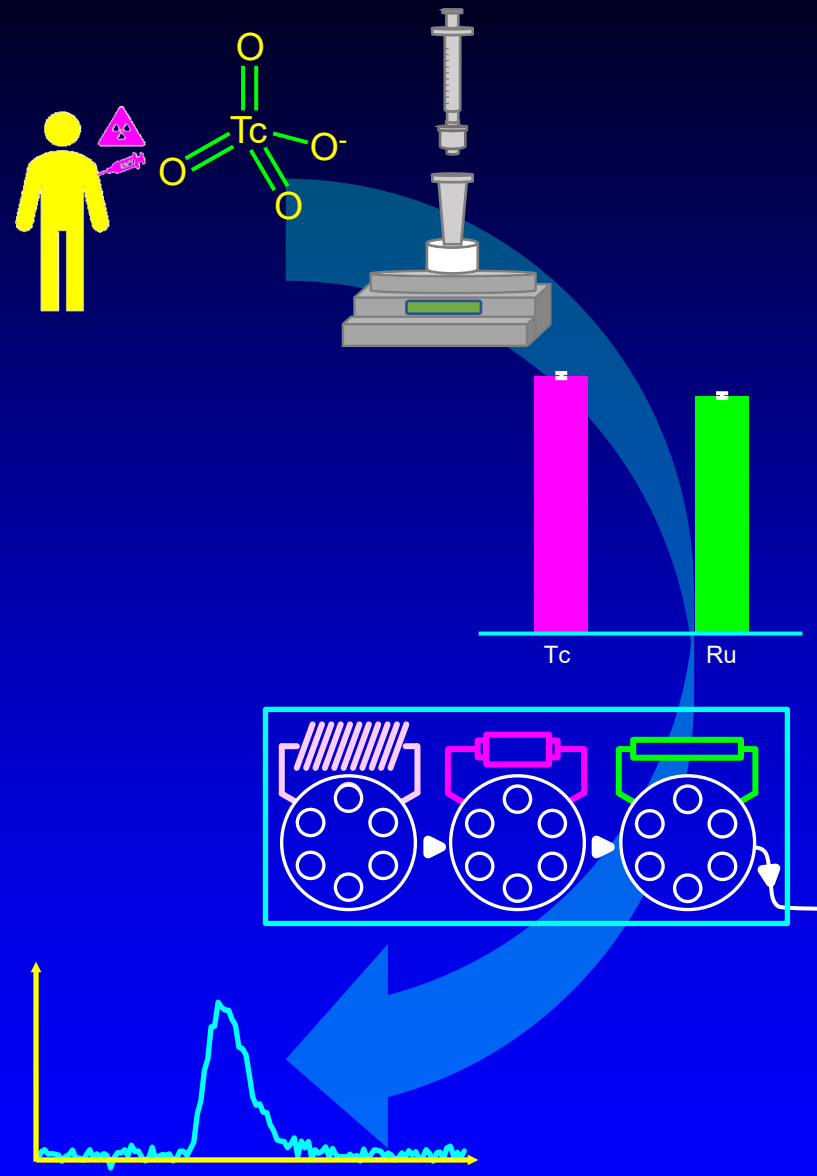
- Vacuum-loading of spiked water sample onto filter disc
- Eluting filter disc with up to 100mL of eluent
- “Rebuffering” of TK201 filter disc eluent back to loading conditions
- Quantification with automated online SPE-IC-ICP-MS method



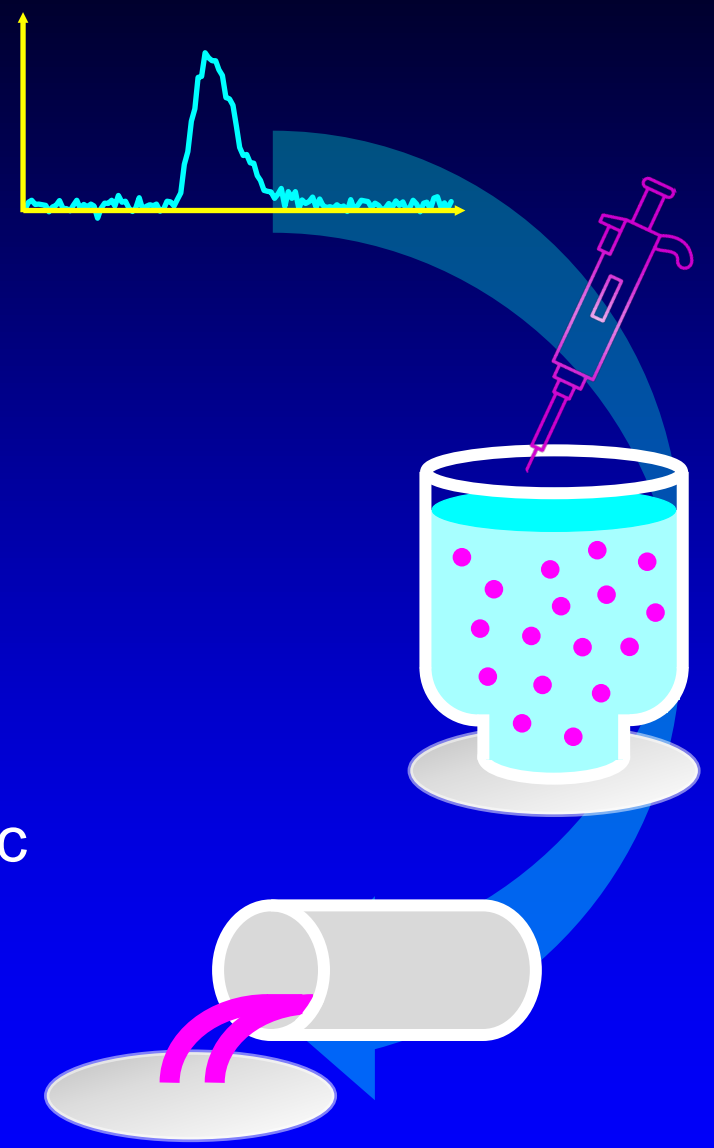
→ Recovery of crucial rebuffering step: 98 %

Conclusion

- Generation of $^{99}TcO_4^-$-standard from medical Tc-generator eluate
- Counter-quantification of $^{99}TcO_4^-$ standard using TXRF
- Automated method for online SPE and IC separation of ^{99}Tc using IBDA
- Quantification of spiked aqueous samples with c(Tc) = 1 and 10 pg/kg



Outlook



- Optimization of offline to online SPE coupling
  - Recovery determination of the full method with spiked sample
- Application of offline SPE method for sampling in difficult locations
- Semi-automated quantification of low concentrated ^{99}Tc in difficult aqueous matrices (e.g. sea water, raw sewage, etc.)

Acknowledgements

TRISKEM
Expertise in Separation Chemistry

European Institute for Molecular Imaging

Elemental Scientific

Renato Margeta

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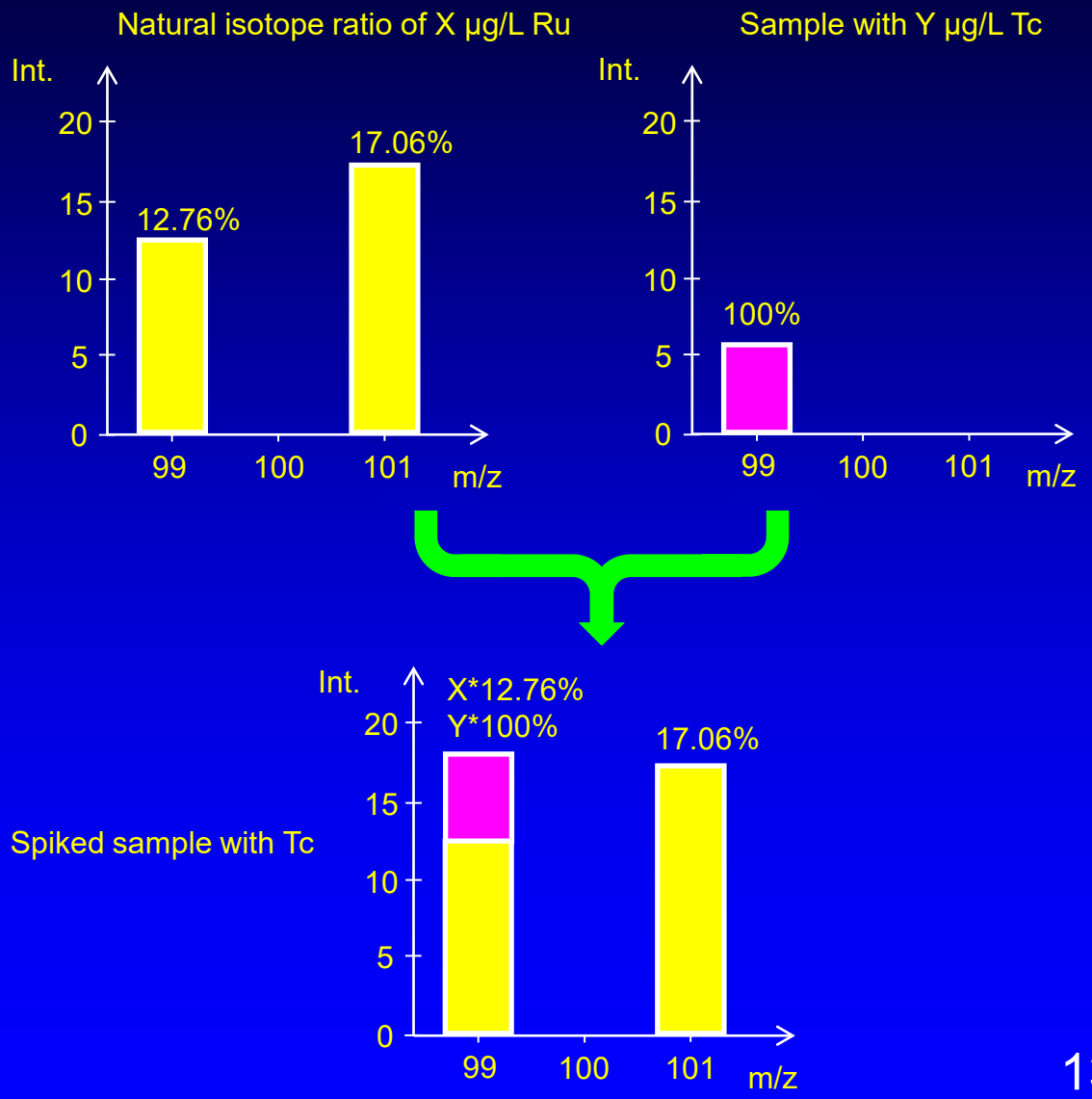
Triskem International UGM – Teddington, 22 February 2023

Quantification Strategy - Isobaric Dilution Analysis

$$c_S = c_{Sp}\frac{m_{Sp}}{m_S}\frac{M_S}{M_{Sp}}\frac{A_b^{Sp}}{A_a^S}\left(\frac{R_m - \frac{A_a^{Sp}}{A_b^{Sp}}}{1 - R_m \cdot \frac{A_b^S}{A_b^S}}\right)$$

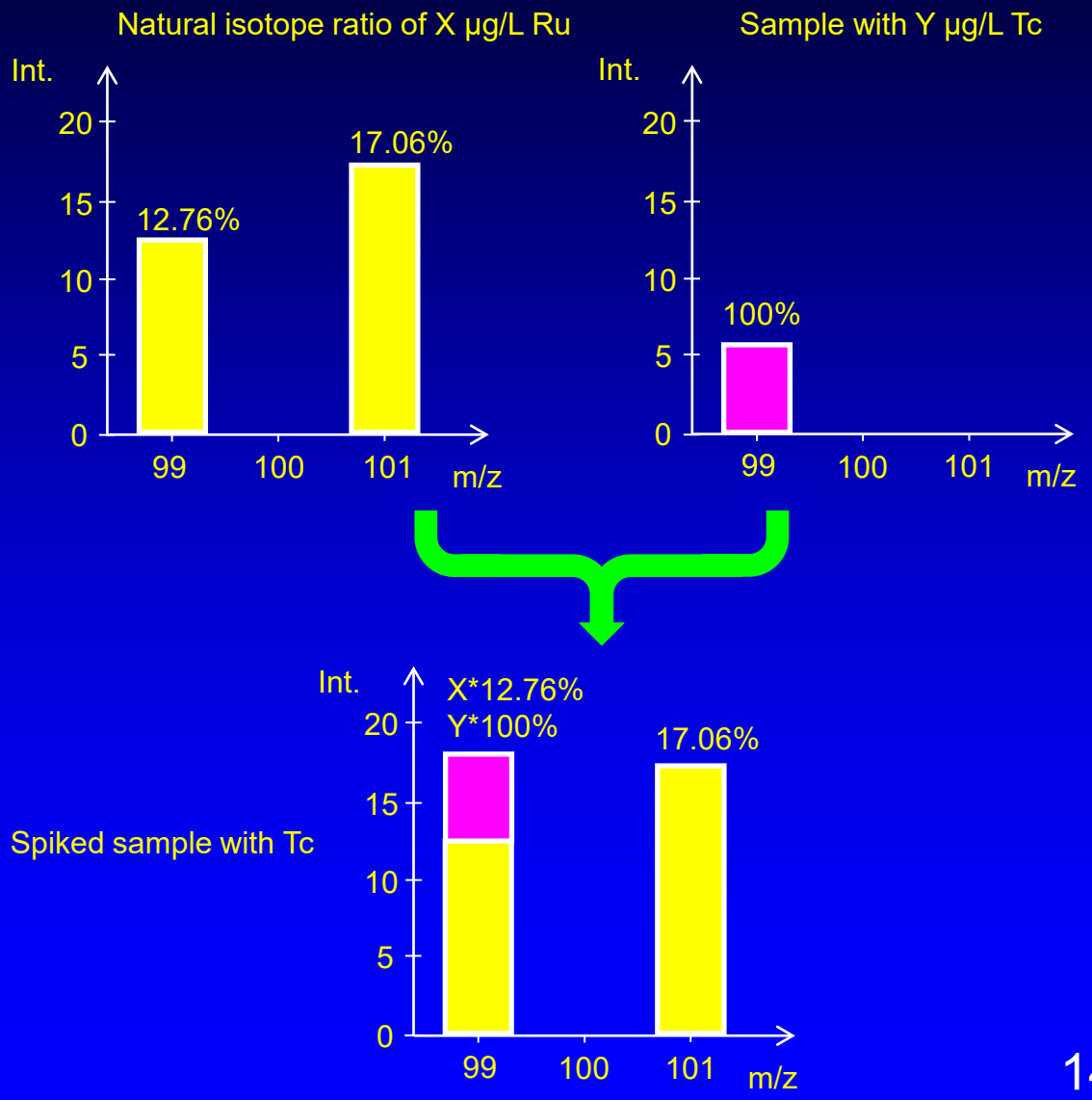


Quantification Strategy - Isobaric Dilution Analysis

$$c_S = c_{Sp}\frac{m_{Sp}}{m_S}\frac{M_S}{M_{Sp}}\frac{A^{Sp}_{101}}{A^{S}_{99}}\left(R_m - \frac{A^{Sp}_{99}}{A^{Sp}_{101}}\right)$$

$$R'_m = \frac{F_r \cdot \left(I^m_{99} - I^m_{101} \cdot \frac{A_{99_{Ru}}}{A_{101_{Ru}}}\right) + I^m_{101} \cdot \frac{A_{99_{Ru}}}{A_{101_{Ru}}}}{I^m_{101}}$$

$$F_r = \frac{r_{Ru}}{r_{Tc}}$$



Application in automated online-IBDA – prep*Fast* IC

- Online SPE - IC separation of spiked aqueous sample with c(Tc) = 10 pg/kg