Application of ICP-MS for U and Pu measurement

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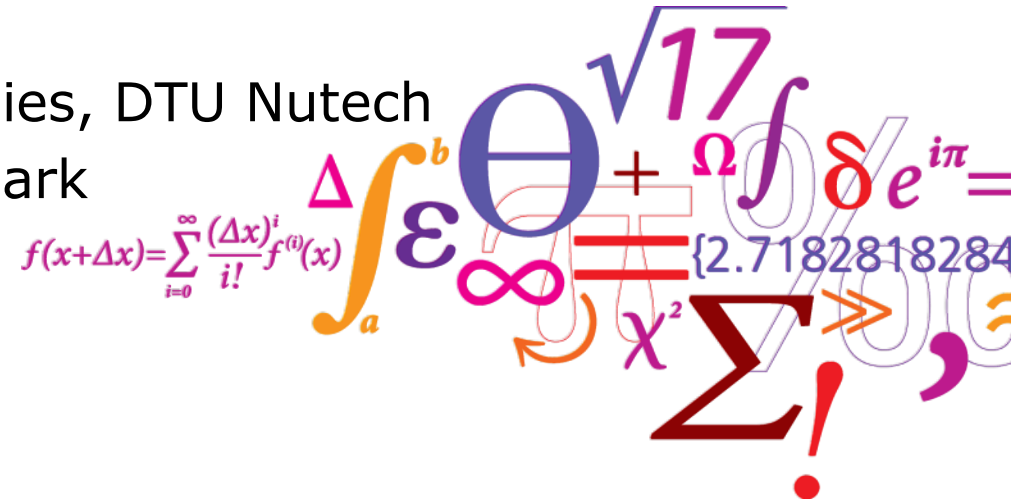

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Outline

- **Inter-comparison exercise for Pu and U determination by ICP-MS**
- **Direct measurement of ^{238}U in seawater by ICP-MS**
- **Conclusion**

Inter-comparison exercise ----Acknowledgement

- Per Roos, Technical University of Denmark (DTU), Denmark
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- Karl Andreas Jensen, Lindis Skipperud, Norwegian University of Life Sciences (NMBU), Norway

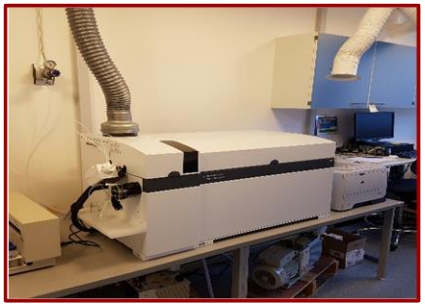
Inter-comparison exercise

- 1) ICP-MS measurement for plutonium isotopes (^{239}Pu and ^{240}Pu) concentrations and isotopic ratio.
- Material: IAEA-384 Fangataufa Lagoon sediment

- *Centralized Purification ---measurement*
- *Individual purification ----measurement*

- 2) ICP-MS measurement for uranium isotopic ratios ($^{234}U/^{235}U$, $^{235}U/^{238}U$ and $^{234}U/^{238}U$)
- Material: NBL CRM 103-A Pitchblende Ore – Silica Mixture Uranium Standard

- *Dissolution ---dilution---measurement*




	Lab A	Lab B		Lab C		Lab D		Lab E	Lab F
Instrument model	Agilent 8800 ICP-QQQ	Element XR ICP-SFMS		Element XR ICP-SFMS		MC-ICP-MS	AttoM double-focusing ICP-SFMS	Element 2 ICP-SFMS	Agilent 8800 ICP-QQQ
Radionuclides	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U	^{239}Pu, ^{240}Pu, ^{242}Pu, ^{238}U	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu	^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{242}Pu
Nebulizer	MicroMist (Borosilicate glass)	Conikal nebulizer	Conikal nebulizer	MicroMist nebulizer	PFA nebulizer	Meinhard and Desolvating nebulizer (DSN)	Meinhard nebulizer	PFA-ST	MicroMist quartz
Typical sensitivity, cps/ppq ^{238}U	0.7	2	1.8	1.2	6	2	2	0.8	1.5 with s-lens
UH^+/U^+	1/14892	1/104000	1/104000		1/100000		No available		None

Seven ICP-MS instruments: two ICP-QQQ, one MC-ICPMS and four ICP-SFMS

Inter-comparison exercise for ^{239}Pu

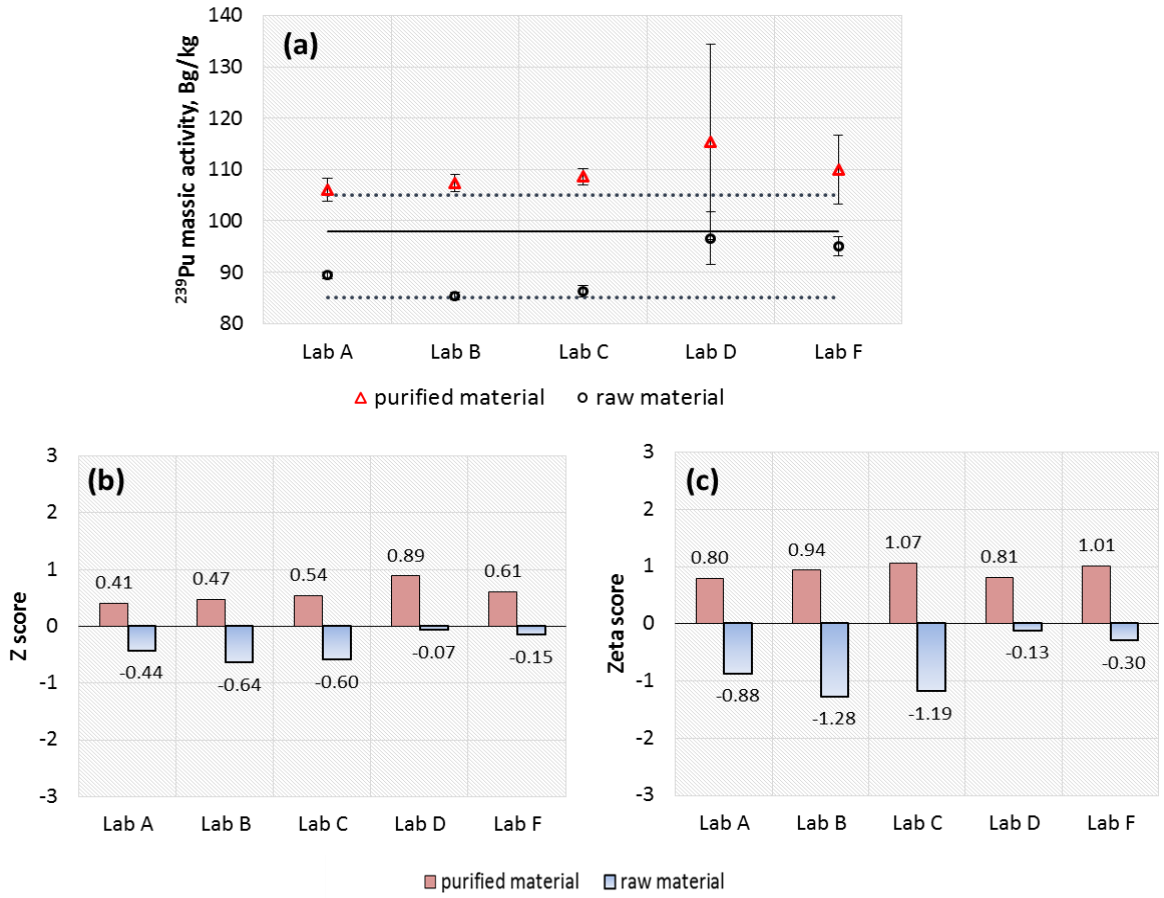


Figure 1 ^{239}Pu massic activities (a), *Z*-score (b) and *Zeta*-score (c) for the reference material IAEA-384.

Inter-comparison exercise for ^{240}Pu

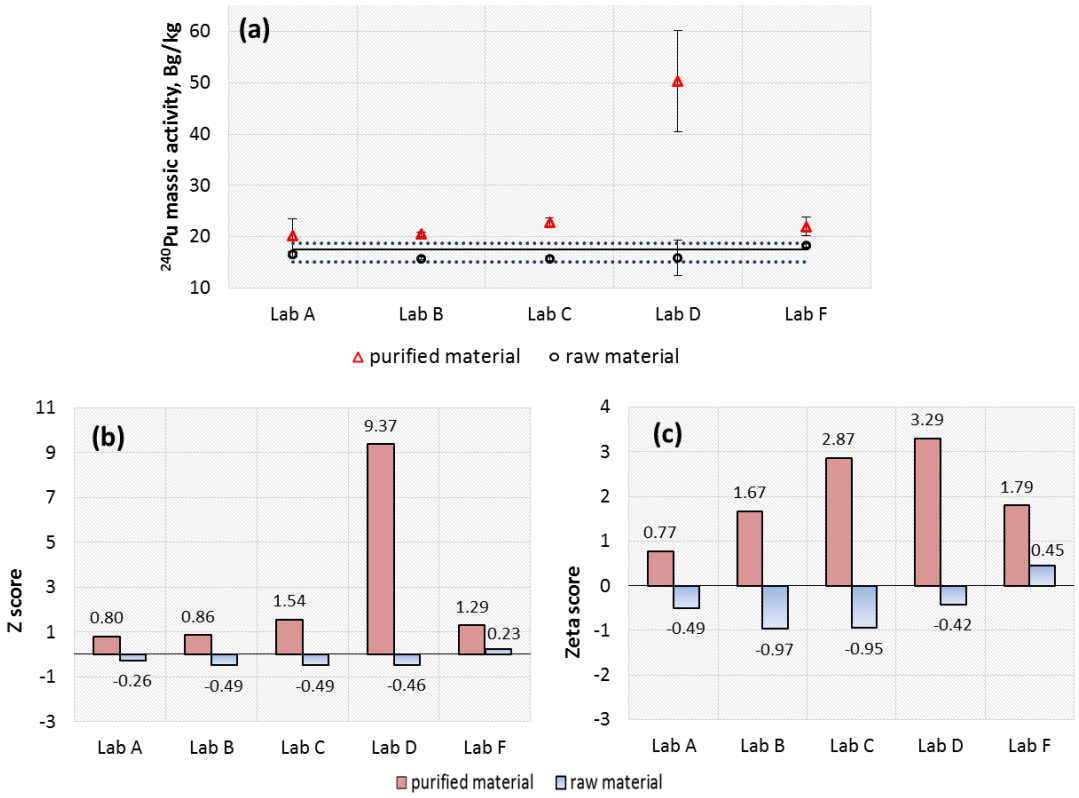


Figure 2 ^{240}Pu massic activitie (a), *Z*-score (b) and *Zeta*-score (c) obtained for the reference material IAEA-384.

Inter-comparison exercise for $^{240}Pu/^{239}Pu$

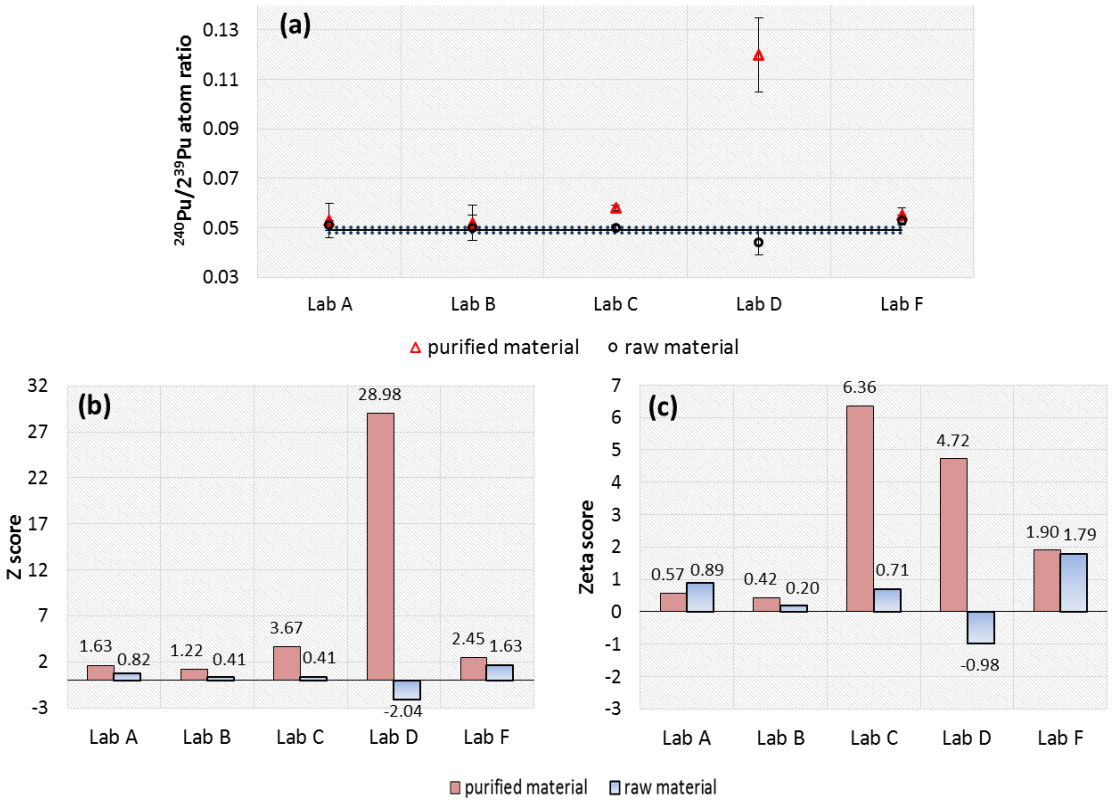


Figure 3 $^{240}Pu/^{239}Pu$ atomic ratio (a), *Z*-score (b) and *Zeta*-score (c) obtained for the reference material IAEA-384.

Inter-comparison exercise for $^{234}U/^{235}U$

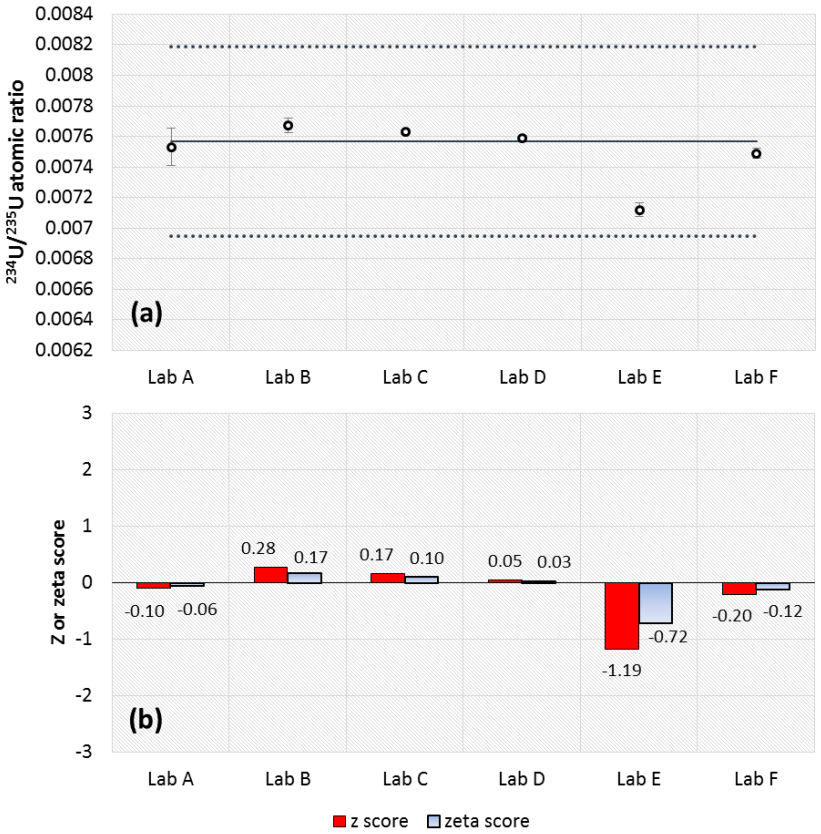


Figure 4 $^{234}U/^{235}U$ isotope ratio (a) and *z*-score and *zeta*-score (b) calculated from the measurement of the reference material NBL CRM 103-A.

Inter-comparison exercise for $^{234}U/^{238}U$

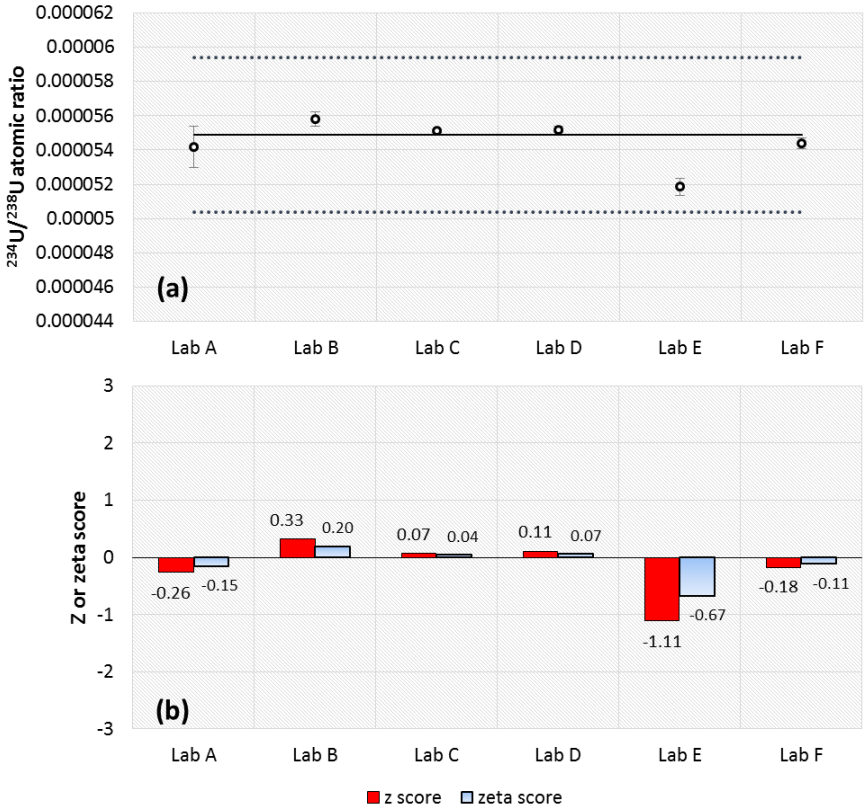


Figure 5 $^{234}U/^{238}U$ isotope ratio (a) and *z*-score and *zeta*-score (b) calculated from the measurement of the reference material NBL CRM 103-A.

Inter-comparison exercise for $^{235}U/^{238}U$

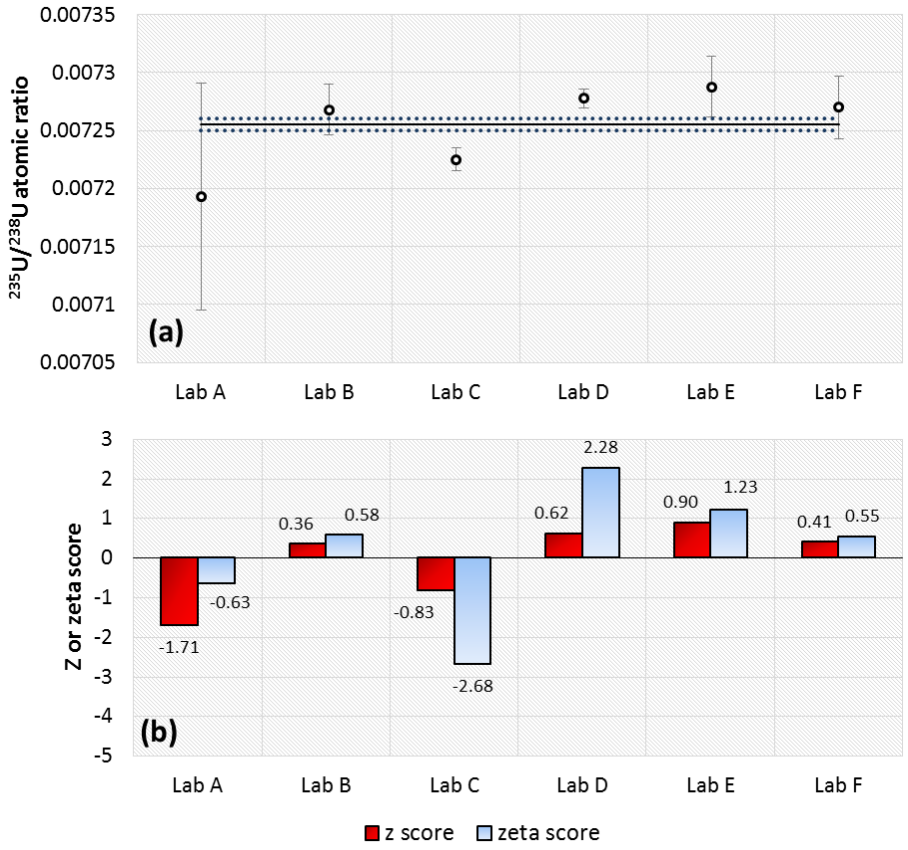


Figure 6 $^{235}U/^{238}U$ isotope ratio (a) and *z*-score and *zeta*-score (b) calculated from the measurement of the reference material NBL CRM 103-A.

Outline

- Inter-comparison exercise for Pu and U determination by ICP-MS

- **Direct measurement of ^{238}U in seawater by ICP-MS**

- Conclusion

Direct measurement of ^{238}U in seawater by ICP-MS

Objective of the work:

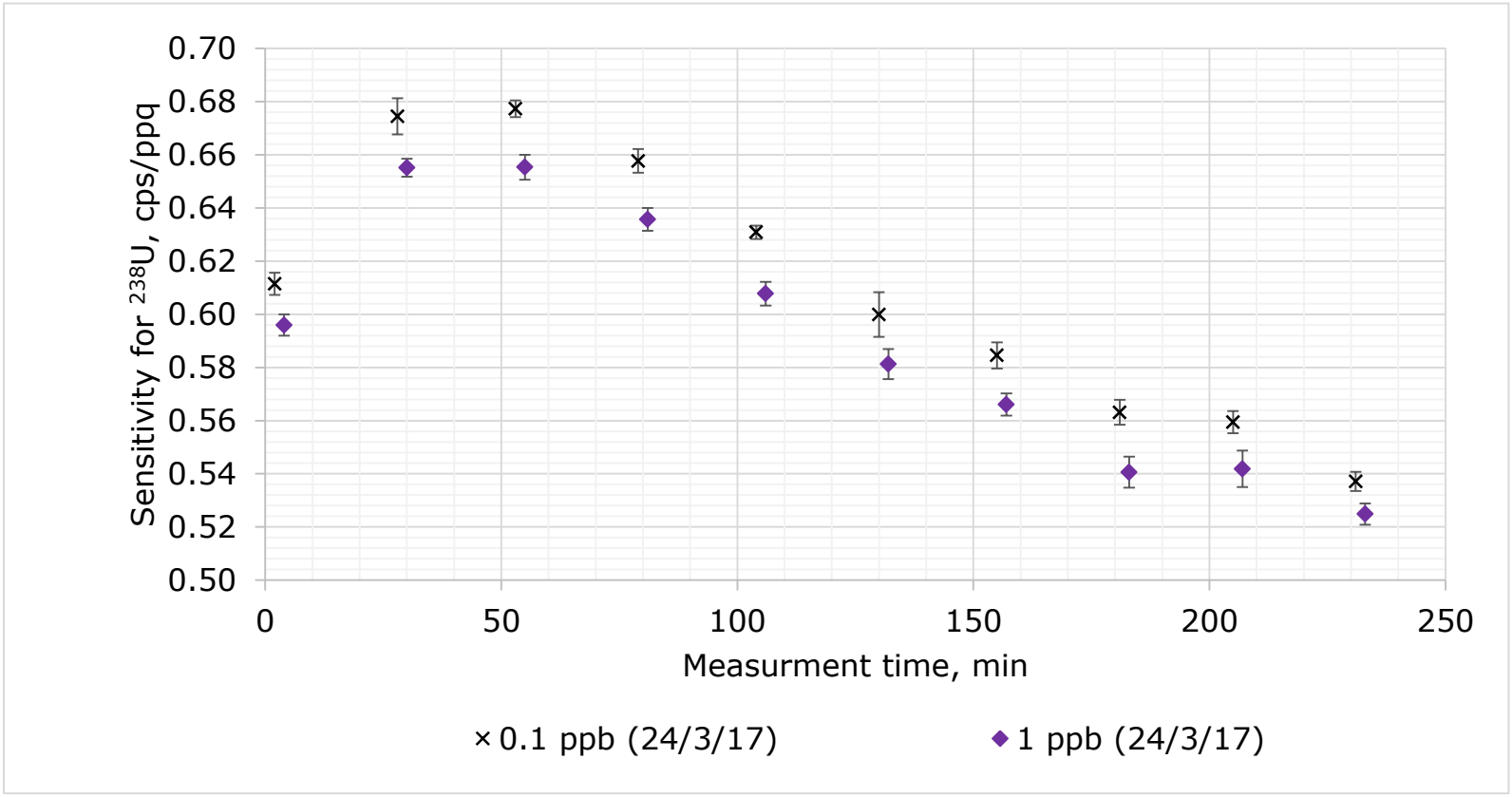
To establish a rapid method for ^{238}U measurement in seawater for tracer studies

Strategy:

Dilution of seawater --- direct measurement by ICP-MS

Direct measurement of ^{238}U in seawater by ICP-MS

Variation of sensitivity with time



Selection of quantitation analysis approach

Isotopic dilution, internal/external standardization

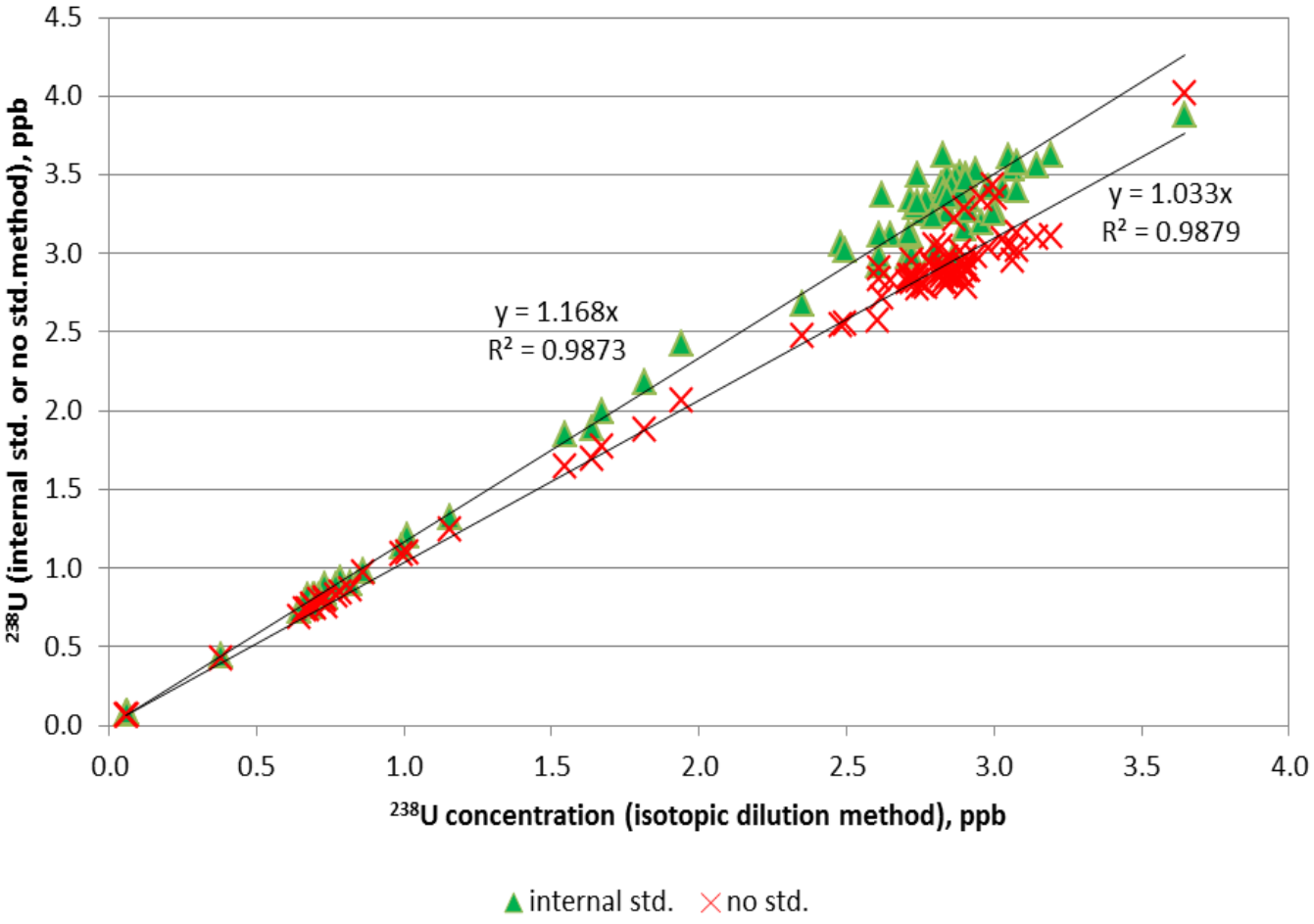
Results of ^{238}U in IAEA-381 seawater by ICP-MS measurement

Dilution factor	Item	^{238}U-isotopic dilution (^{233}U), ppb	Bias, %	^{238}U-external standardization, ppb	Bias, %	^{238}U-internal standardization (^{115}In), ppb	Bias, %
10	**Average**	**3.16**	**-6.7**	**2.31**	**-31.7**	**3.70**	**9.1**
	SD	0.04		0.11		0.17	
20	**Average**	**3.30**	**-2.8**	**2.87**	**-15.3**	**3.32**	**-2.0**
	SD	0.03		0.14		0.03	
50	**Average**	**3.52**	**3.7**	**3.44**	**1.6**	**3.70**	**9.0**
	SD	0.13		0.21		0.22	

Our recommendation: 20-50 dilution, isotopic dilution

Selection of quantitation analysis approach

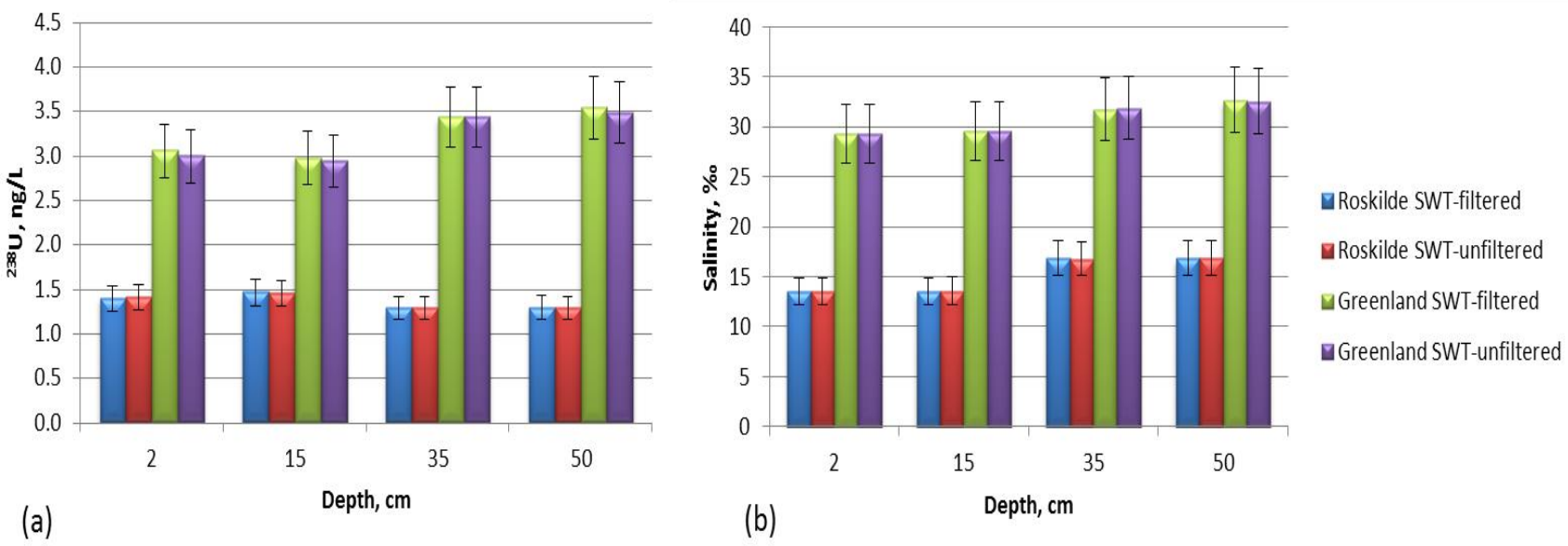
Isotopic dilution, internal/external standardization



- 112 seawater (0.1-3.7 ppb U)
- 50-time dilution

Sample representativeness

Evaporation, condensation??



Awareness should be paid when take small volume from bulk sample after long-term storage

Conclusion

- ***Inter-comparison exercise:***
- The U isotopic ratios measurement was generally well performed in all labs, whereas high-resolution sector filed ICP-MS is preferred option for high precision.
- The purity of the Pu fraction affect the accuracy of the results and special care need to be paid on the existence of interfering nuclides which could possibly induce large analytical error in the measurement.

- ***Direct measurement of ^{238}U in seawater:***
- Isotope dilution is more accurate compared to internal/external standardization.
- Appropriate dilution is important to minimize the matrix effect and 20-50 times is recommended.
- Sensitivity decreases after continuous measurement of seawater samples due to the slow blockage of the introduction pathway.
- Cautions need to be paid in sampling representativeness for long-term stored large volume samples.

Thanks for your attention!

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