URANIUM AND THORIUM-ISOTOPES RADIOCHEMICAL SEPARATION AND QUANTIFICATION OF NORM SAMPLES BY ALPHA-SPECTROMETRY

NÚRIA CASACUBERTA

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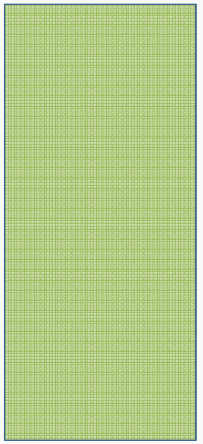
5th EAN_{NORM} WORKSHOP - 4th December 2012



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OUTLINE

- INTRODUCTION
  - ANALYSIS OF NORM SAMPLES IN OUR LABORATORY
  - WHY URANIUM AND THORIUM ISOTOPES?
  - CLASSICAL METHODS FOR U AND Th SEPARATION
- AIMS OF THIS STUDY
- MATERIALS, METHODS AND RESULTS
  - LIQUID-LIQUID EXTRACTION vs. EXTRACTION CHROMATOGRAPHY IN ENVIRONMENTAL SAMPLES.
  - EXTRACTION CHROMATOGRAPHY (UTEVA) IN NORM SAMPLES.
  - REUSE OF UTEVA COLUMNS FOR THE ANALYSIS OF NORM SAMPLES.
- CONCLUSIONS.

NORM SAMPLES: LABORATORY ANALYSIS

SAMPLING

LABORATORY

^{238}U, ^{234}U, ^{235}U

^{232}Th, ^{230}Th

Radiochemistry + PIPS detectors

^{226}Ra (and γ emitters)

Gemma detectors

^{210}Pb, ^{210}Po

Radiochemistry + PIPS detectors

NORM SAMPLES: LABORATORY ANALYSIS

SAMPLING

LABORATORY

^{238}U, ^{234}U, ^{235}U

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^{226}Ra (and γ emitters)

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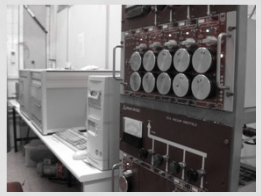
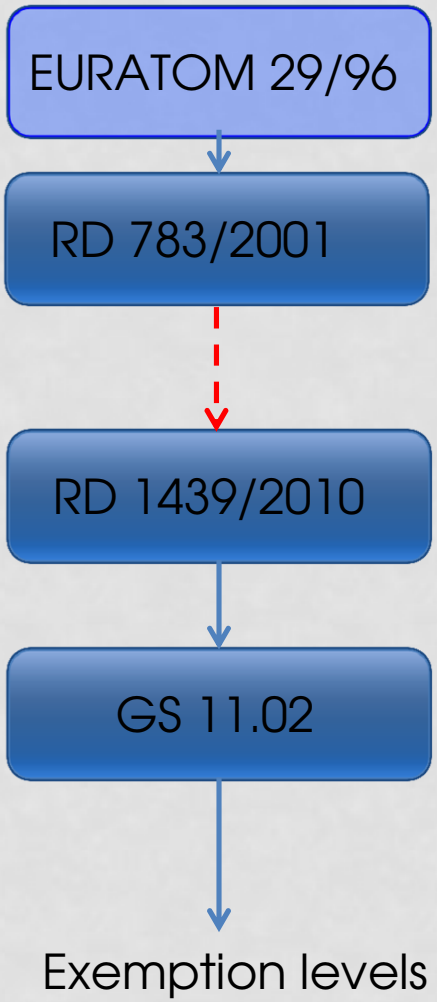


URANIUM AND THORIUM IN NORM SAMPLES (SPANISH LEGISLATION)



Anexo A Niveles de exención/desclasificación en kBq/kg (Bq/g)

Radionucleido	Todos los materiales	Lodos húmedos de industrias de petróleo y gas
U-238 (sec) incl. U-235 (sec)	0,5	5
U natural	5	100
Th-230	10	100
Ra-226+	0,5	5
Pb-210+	5	100
Po-210	5	100
U-235 (sec)	1	10
U-235 +	5	50
Pa-231	5	50
Ac-227+	1	10
Th-232 (sec)	0,5	5
Th-232	5	100
Ra-228+	1	10
Th-228+	0,5	5
K-40	5	100

CLASSICAL METHODS FOR U AND TH DETERMINATION

- Liquid-liquid extraction
- Anion exchange resins

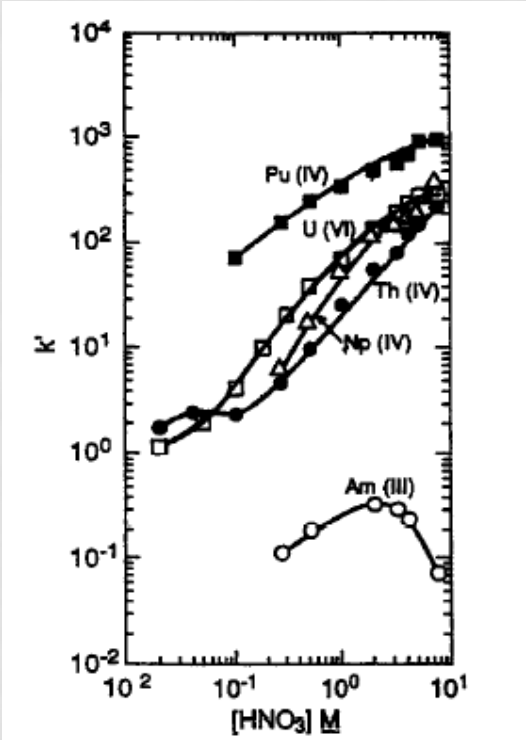
URANIUM PURIFICATION:

- from Rare Earth Elements.
- from Th isotopes.
- from interferring elements: Fe, Ca, Na.

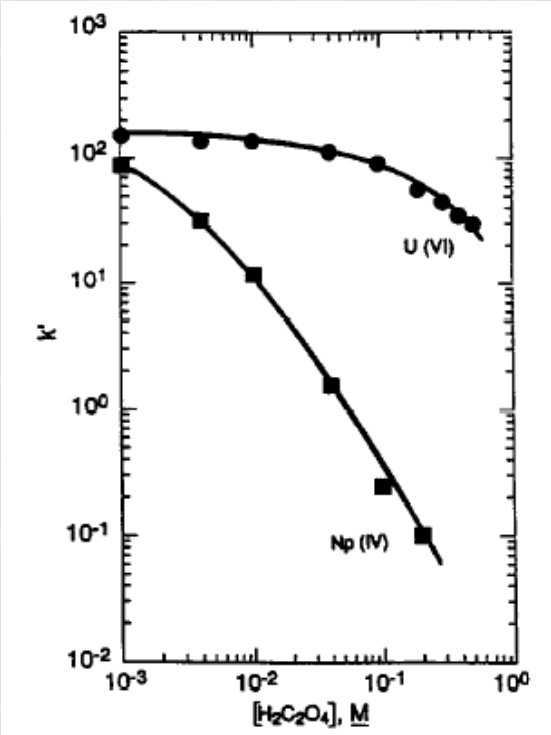
- Time consuming.
- Generate substantial volumes of organic-waste.
- Have limited effectiveness in removing certain common matrix components (e.g. Iron)

AN ALTERNATIVE MATERIAL: DIAMYL AMYLPHOSPHONATE

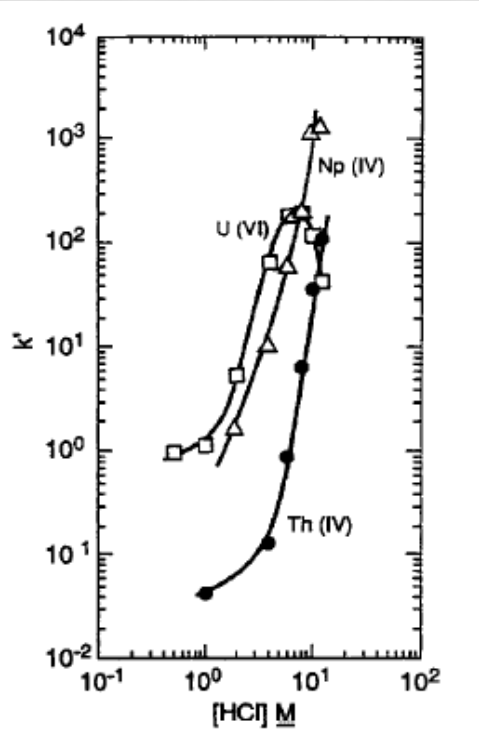
Horwitz et al. (1992; 1995)



1) High U and Th retention in low molarity HNO_3



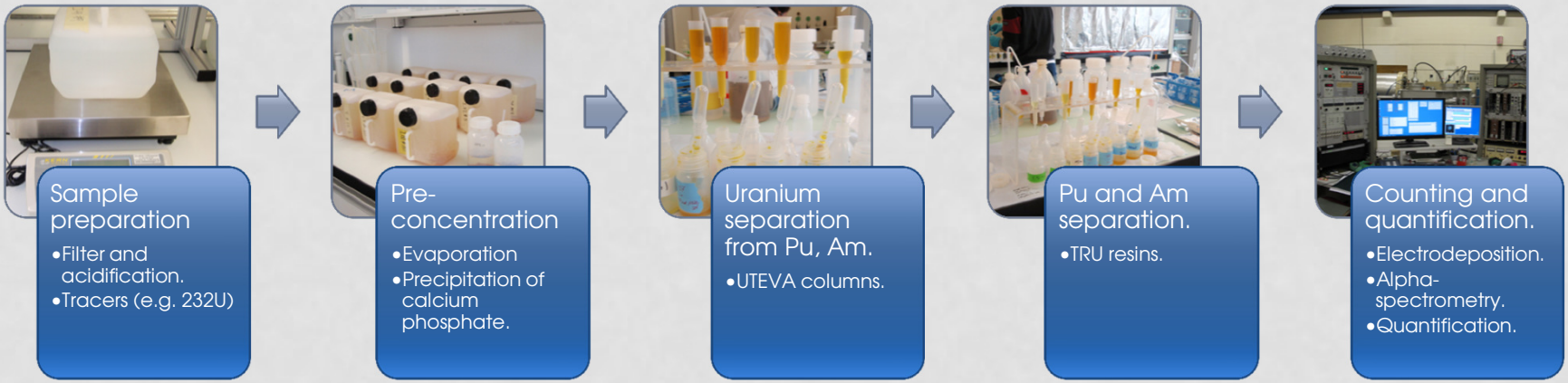
2) High U retention at low oxalic acid molarity.



3) Th elution at high HCl molarity.

EXTRACTION CHROMATOGRAPHY USING UTEVA COLUMNS (EICHROM)

Horwitz et al. (1992; 1995)



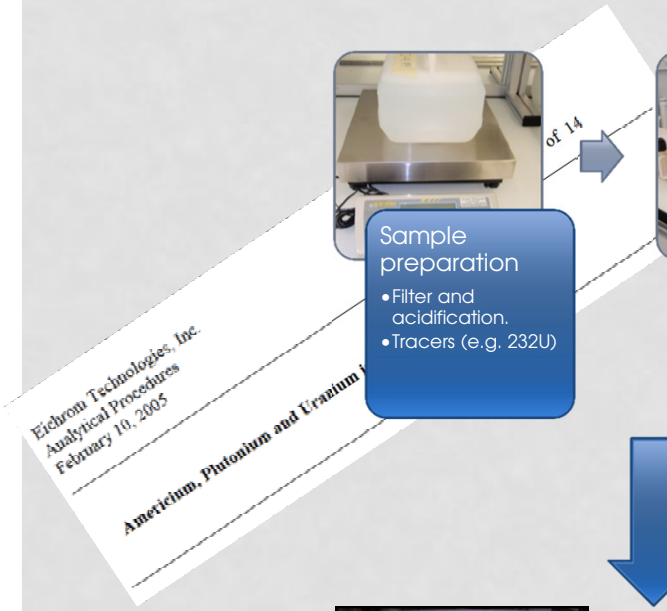
- Simple and effective method for separation and pre-concentration of U from aquous solution.
- Other components such as Na, Fe and Ca are unretained in the resin.
- Encouraged its application (e.g. in nuclear waste).

AIMS OF THIS STUDY

- Extraction chromatography as an alternative method for U and Th determination in NORM samples.

- Specific aims:
  - Compare extraction chromatograpy with liquid-liquid extraction (TBP) in environmental samples.
  - Adapt the method publised by Eichrom for the quantification of Th isotopes in NORM samples
  - Test the cleaning of the UTEVA columns after its usage.

EXTRACTION CHROMATOGRAPHY ADAPTED TO NORM SAMPLES



Sample preparation
- Filter and acidification.
- Tracers (e.g. 232U)

Pre-concentration
- Evaporation
- Precipitation of calcium phosphate.

Uranium separation from Pu, Am.
- UTEVA columns.

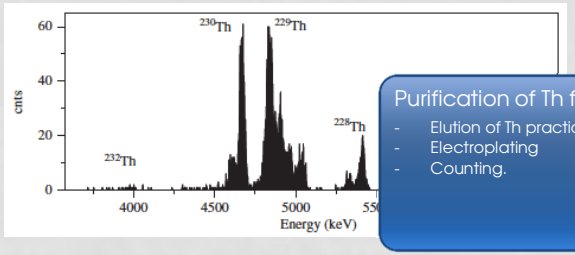
Pu and Am separation.
- TRU resins.

Counting and quantification.
- Electrodeposition.
- Alpha-spectrometry.
- Quantification.

✗

✓

Solid and liquid samples (NORM)
- Digestion.
- Tracers (232U and 229Th)



Purification of Th from U.
- Elution of Th praction.
- Electroplating
- Counting.

LIQUID-LIQUID EXTRACTION VS. EXTRACTION CHROMATOGRAPHY

SAMPLES ANALYZED:

- Reference materials
  - Liquid: IAEA-2008-03.
  - Solid: phosphogypsum IAEA-2008-.
- Environmental samples:
  - Water
    - Surface river samples (Guadalquivir).
    - Underground waters (uraniunm mining Spain)
  - Sediment
    - Riverbed sediment samples.

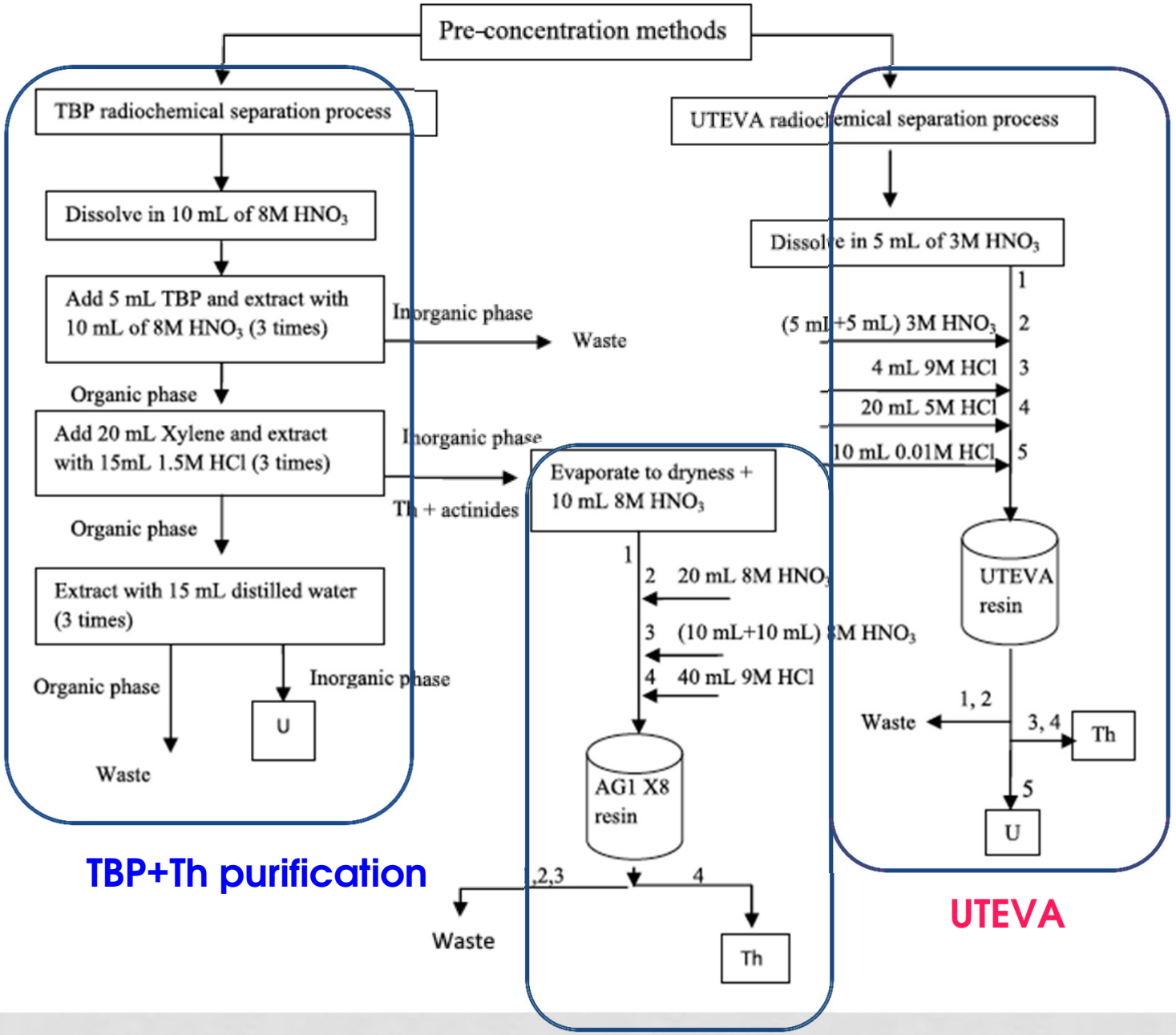
ANALYTICAL METHODS:

- LIQUID-LIQUID SOLVENT EXTRACTION (TBP).
- EXTRACTION CHROMATOGRAPHY (UTEVA).

EVALUATION CRITERIA:

$$Z\text{-score} = \frac{\text{Value}_{\text{reported}} - \text{Value}_{\text{target}}}{0.10\ \text{Value}_{\text{target}}}$$

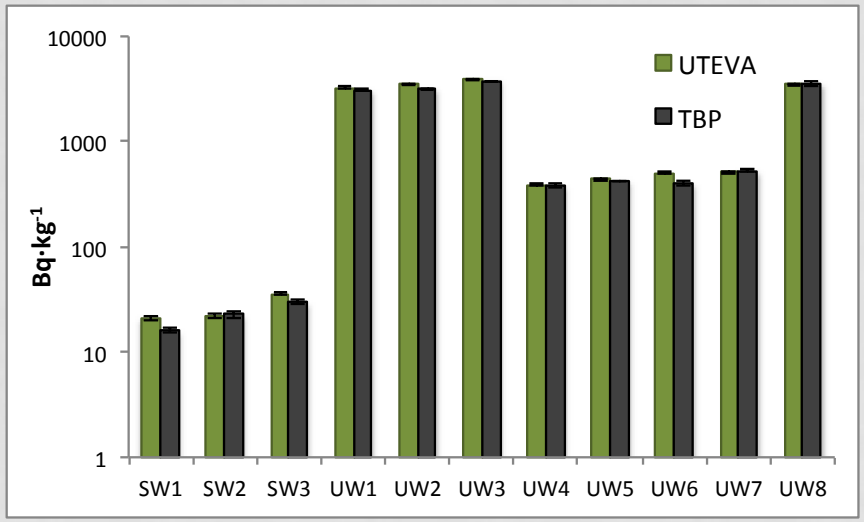
where "$\text{Value}_{\text{reported}}$" means the obtained result using UTEVA procedure and "$\text{Value}_{\text{target}}$" is the reference value in the standard or reference sample. If $|Z\text{-score}| \leq 2$, the reported value will be considered as satisfactory; it would be questionable if $|Z\text{-score}| \leq 3$; and unsatisfactory if $|Z\text{-score}| \geq 3$.


Pre-concentration methods
TBP radiochemical separation process
Dissolve in 10 mL of 8M HNO3
Add 5 mL TBP and extract with 10 mL of 8M HNO3 (3 times)
Inorganic phase
Waste
Organic phase
Add 20 mL Xylene and extract with 15mL 1.5M HCl (3 times)
Inorganic phase
Th + actinides
Organic phase
Extract with 15 mL distilled water (3 times)
Organic phase
Inorganic phase
U
Waste
TBP+Th purification
Evaporate to dryness + 10 mL 8M HNO3
1
2 20 mL 8M HNO3
3 (10 mL+10 mL) 8M HNO3
4 40 mL 9M HCl
AG1 X8 resin
1,2,3
4
Waste
Th
UTEVA radiochemical separation process
Dissolve in 5 mL of 3M HNO3
1
(5 mL+5 mL) 3M HNO3 2
4 mL 9M HCl 3
20 mL 5M HCl 4
10 mL 0.01M HCl 5
UTEVA resin
1, 2
Waste
3, 4
Th
5
U
UTEVA

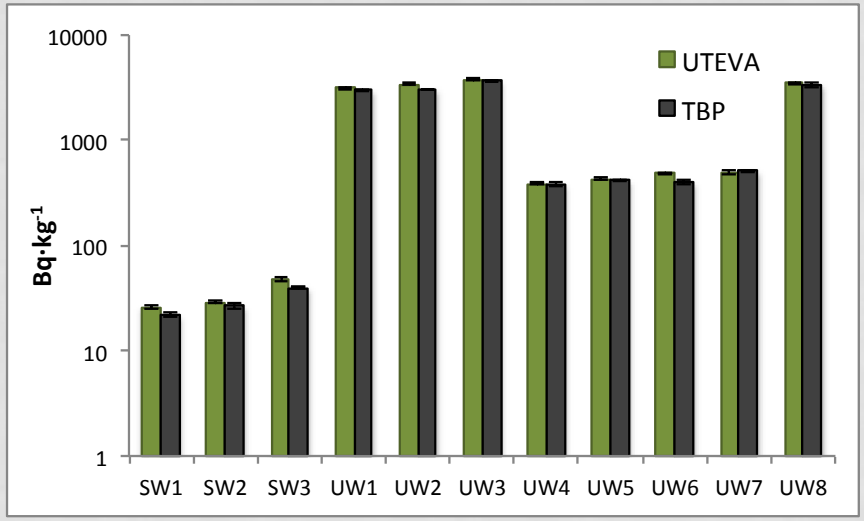
LIQUID-LIQUID EXTRACTION VS. EXTRACTION CHROMATOGRAPHY

URANIUM in WATERS

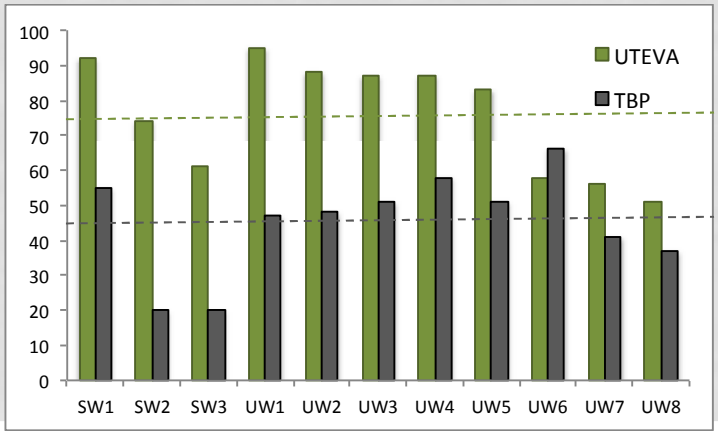
^{238}U



^{234}U



CHEMICAL YIELD



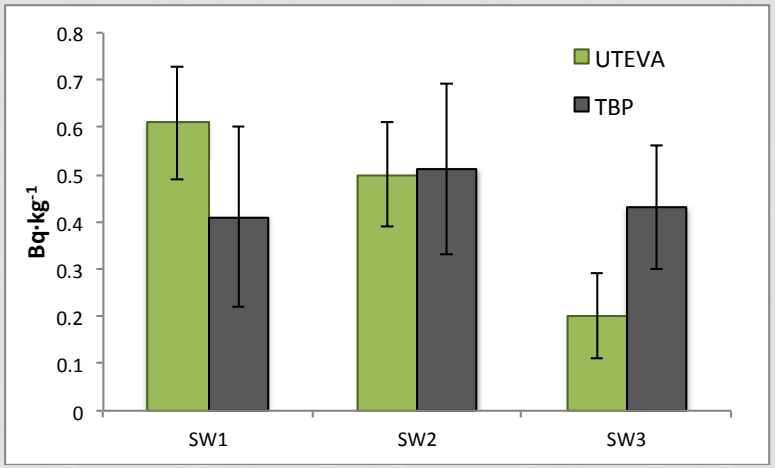
UTEVA: 76%

TBP: 45%

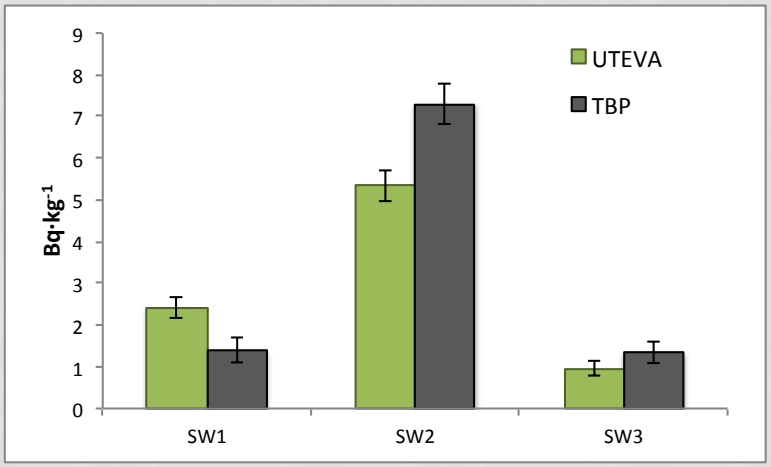
LIQUID-LIQUID EXTRACTION VS. EXTRACTION CHROMATOGRAPHY

THORIUM in WATERS

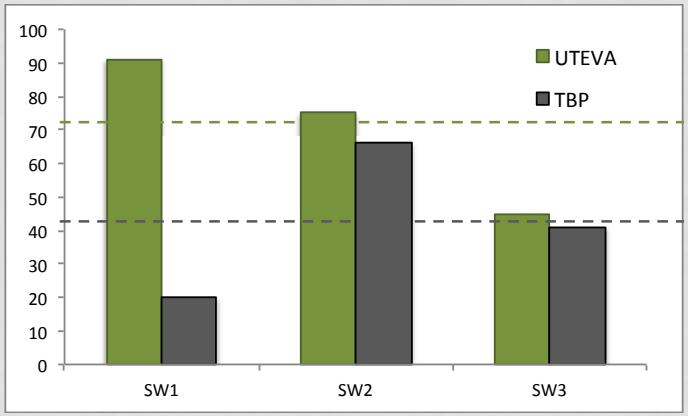
^{232}Th



^{230}Th



CHEMICAL YIELD



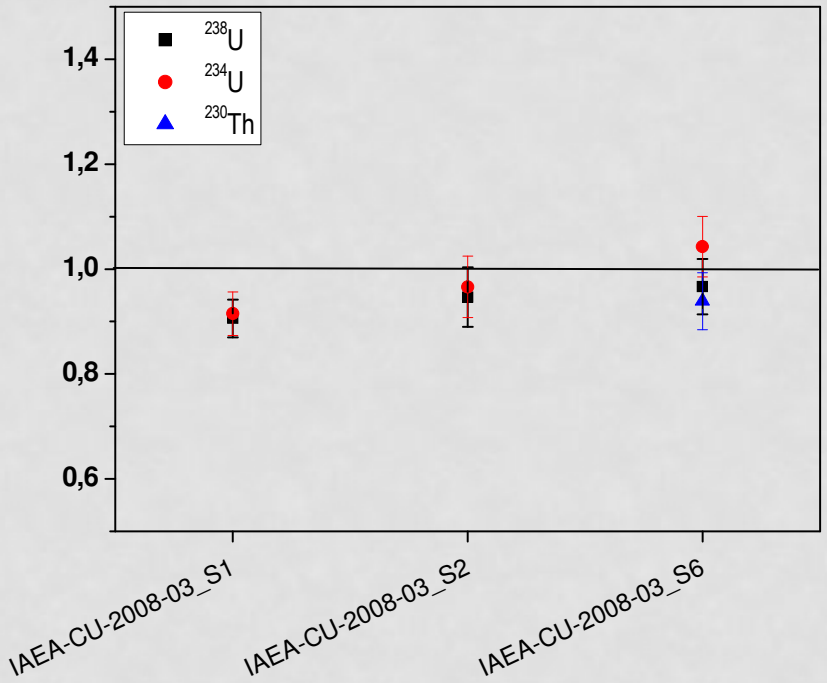
UTEVA: 70%

TBP: 42%

EVALUATION CRITERIA OF EXTRACTION CHROMATOGRAPHY

IAEA-2008-03 proficiency test

i) **Liquid samples S1 and S2 (1 replicate)**
ii) **Phosphogypsum S6 (3 replicates)**



i) **Good accuracy: Low Relative bias was (3-9%).**
ii) **Z-score < 1**
iii) **u-score < 2.58**

LIQUID-LIQUID EXTRACTION VS. EXTRACTION CHROMATOGRAPHY

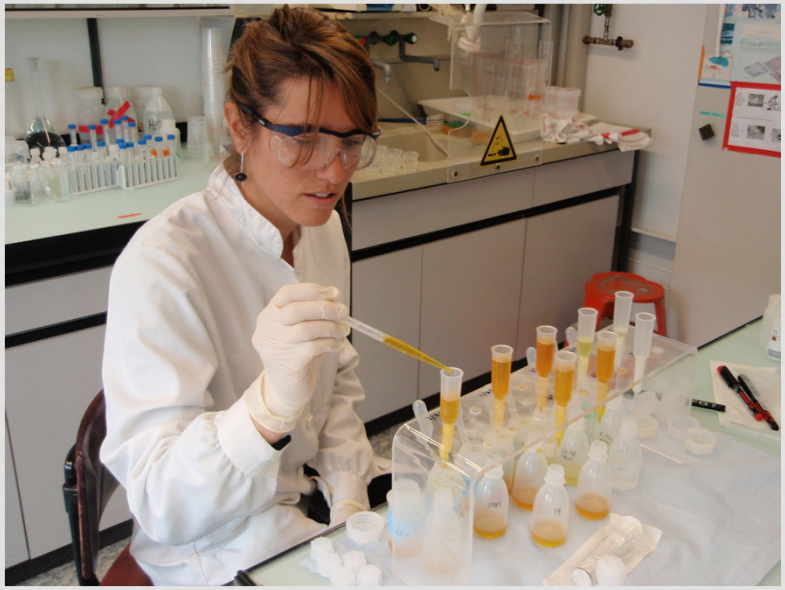
ADVANTAGES OF EXTRACTION CHROMATOGRAPHY vs. LIQUID-LIQUID SOLVENT EXTRACTION

Concept	TBP+Th purification	UTEVA
Time separation process	4 hours (2 h TBP + 2 h Th purification)	2 hours ✓
Reagents needed	5 mL TBP 20 mL xylene 80 ml 8M HNO_3 45 mL distilled H_2O 7.5 g AG1X8 resin	15 mL 3M HNO_3 (4 mL 9M+20 mL 5M+10 mL 0.01M) HCl 1 UTEVA column ✓
Generated Wastes	5 mL TBP 29 mL Xylene 30 mL 8M HNO_3 7.5 g AG1X8 resin	15 mL 3M HNO_3 UTEVA column ✓

EXTRACTION CHROMATOGRAPHY (UTEVA) IN NORM SAMPLES

SAMPLES ANALYZED:

- Phosphate industry (DCP production):
  - Phosphate rock.
  - Sludges.
  - Dicalcium phosphate.



ANALYTICAL METHODS:

- EXTRACTION CHROMATOGRAPHY (UTEVA).

SPECIFIC AIM:

- Test the extraction chromatography adapted method to NORM samples.
- Test the reuse of UTEVA columns after its use.

EXTRACTION CHROMATOGRAPHY (UTEVA) IN NORM SAMPLES

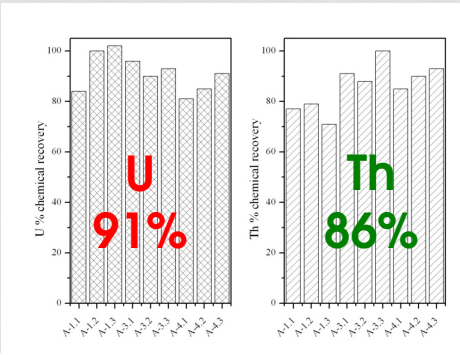
Table 3

Results on the activity concentrations (A), uncertainties (ΔA), average values (Ā) and standard deviation (σ_{n-1}) of NORM samples obtained from a DCP production plant. Uncertainties and standard deviation are expressed in % at 1σ. Chemical yields (ρ) for each sample are also indicated.

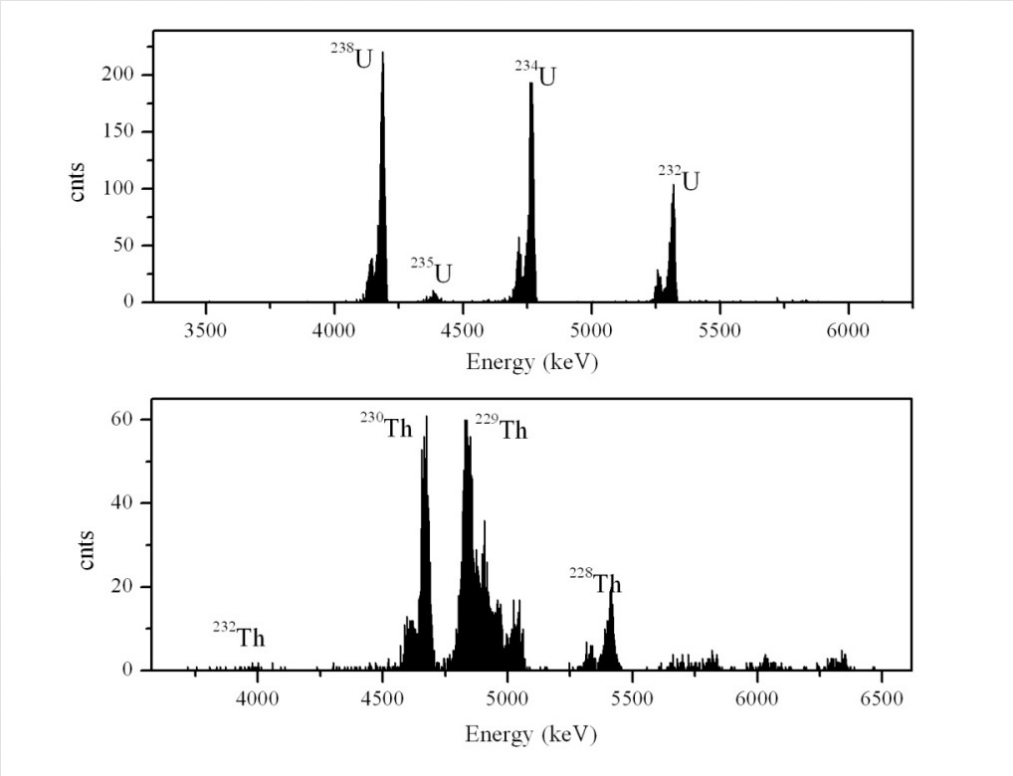
Sample code	^{238}U (Bq kg^{-1})				^{235}U (Bq kg^{-1})				^{234}U (Bq kg^{-1})				ρ (U) %	^{232}Th (Bq kg^{-1})				^{230}Th (Bq kg^{-1})				ρ (Th) %
	A	ΔA (%)	Ā	σ_{n-1} (%)	A	ΔA (%)	Ā	σ_{n-1} (%)	A	ΔA (%)	Ā	σ_{n-1} (%)		A	ΔA (%)	Ā	σ_{n-1} (%)	A	ΔA (%)	Ā	σ_{n-1} (%)	
A-1.1	1733	4	1706	5	53	12	60	15	1697	4	1690	5	84	24	14	22	8	1750	6	1730	3	77
A-1.2	1778	4			58	11			1773	4			100	21	18			1671	6			79
A-1.3	1607	4			70	11			1600	4			102	22	19			1769	6			71
A-3.1	4676	4	5036	7	185	10	193	7	5870	4	6287	6	96	136	8	138	5	10144	5	10,090	8	91
A-3.2	5333	4			186	9			6615	4			90	147	8			10,871	5			88
A-3.3	5098	3			207	6			6375	3			93	132	13			9253	8			100
A-4.1	4017	6	3993	1	161	13	154	4	5451	5	5216	4	81	113	14	119	14	8976	8	8618	4	85
A-4.2	3956	5			153	13			5022	5			85	138	14			8277	8			90
A-4.3	4007	4			147	10			5174	4			91	106	11			8600	6			93

GOOD PRECISION AND REPRODUCIBILITY.

OPTIMUM CHEMICAL RECOVERIES.



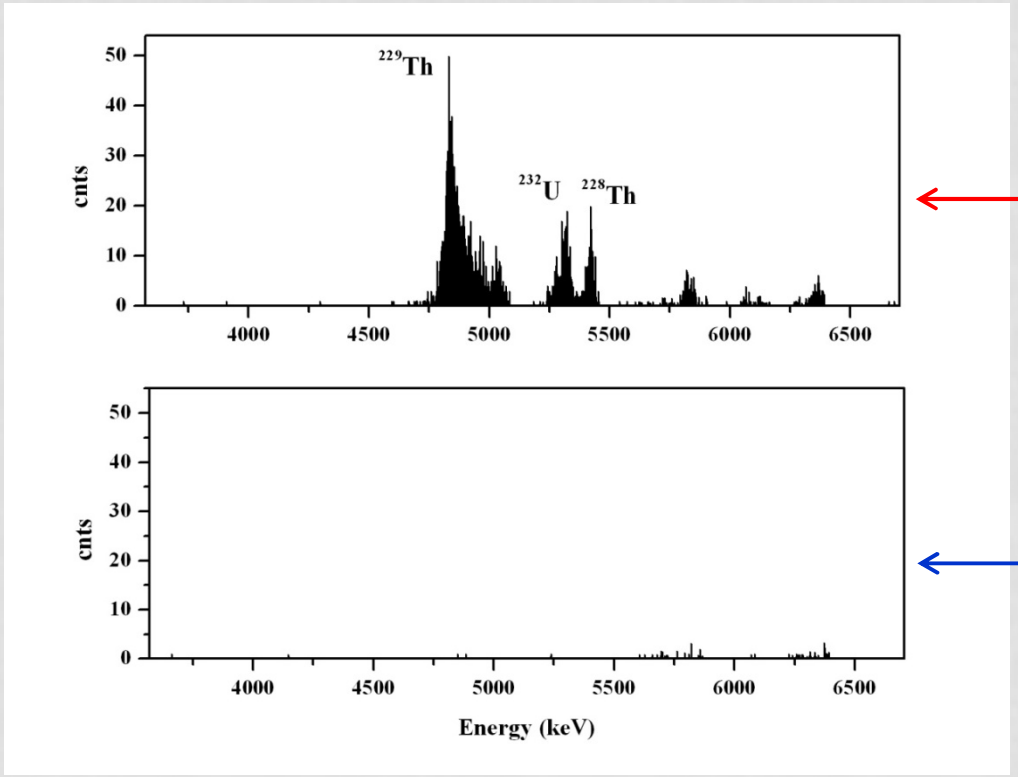
EXTRACTION CHROMATOGRAPHY (UTEVA) IN NORM SAMPLES

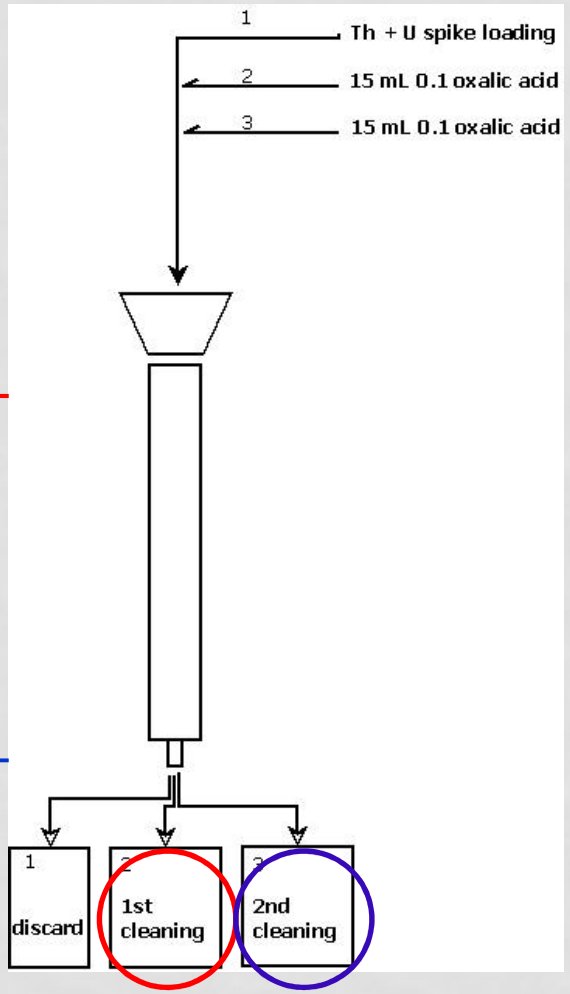


GOOD SPECTRA RESOLUTION
(FWHM = 27 16 keV for ^{238}U and ^{230}Th, respectively)

REUSE OF UTEVA COLUMNS FOR NORM SAMPLES

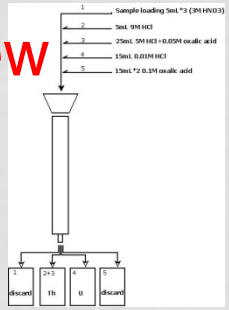
i) 0.1 M Oxalic acid as a cleaning solution:

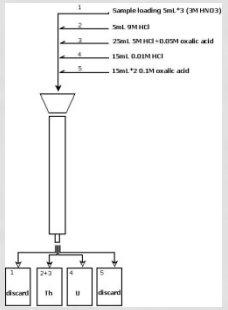


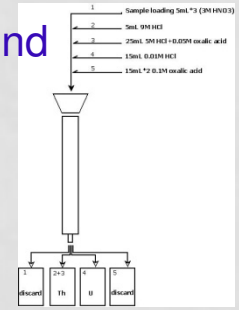


REUSE OF UTEVA COLUMNS FOR NORM SAMPLES

ii) 1st and 2nd UTEVA recycle:

New 

1st 

2nd 

Sample	UTEVA usage	^{238}U (Bqkg^{-1})	^{235}U (Bqkg^{-1})	^{234}U (Bqkg^{-1})	ρ(U)	^{230}Th (Bqkg^{-1})	ρ(Th)
A-1.1	New UTEVA resins	1733 ± 71	53 ± 7	1697 ± 70	84%	1750 ± 101	77%
A-1.2		1778 ± 67	58 ± 6	1773 ± 67	100%	1671 ± 98	79%
A-1.3		1607 ± 64	70 ± 8	1600 ± 63	101%	1769 ± 107	71%
A-1.1R1	1st UTEVA recycle	1695 ± 66	68 ± 7	1603 ± 63	99%	1635 ± 90	66%
A-1.2R1		1692 ± 64	63 ± 7	1645 ± 63	98%	1643 ± 105	11%
A-1.3R1		1700 ± 63	55 ± 6	1628 ± 61	102%	1711 ± 101	49%
A-1.1R2	2on UTEVA recycle	1601 ± 96	64 ± 11	1566 ± 95	97%	1788 ± 95	77%
A-1.2R2		1752 ± 107	55 ± 11	1635 ± 101	98%	1598 ± 93	93%
A-1.3R2		1616 ± 96	58 ± 11	1658 ± 98	102%	1696 ± 95	71%
Average New UTEVA		1706 ± 127	60 ± 13	1690 ± 126	95%	1730 ± 180	76%
Average 1st UTEVA recycle		1696 ± 112	62 ± 12	1625 ± 109	100%	1663 ± 173	42%
Average 2nd UTEVA recycle		1656 ± 179	59 ± 19	1619 ± 172	99%	1647 ± 172	80%

CONCLUSIONS

- Advantages of extraction chromatography (UTEVA) compared to liquid-liquid solvent extraction (TBP):
  - Greater chemical yields for U and Th in extraction chromatography.
  - Remove interferring elements more efficiently.
  - Faster and simpler in its application.
  - Generates less laboratory wastes.
- Extraction chromatography (UTEVA) in NORM samples:
  - Optimum accuracy and precision of the technique.
  - UTEVA resins can be reused at least three times, reducing its economical costs.

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Determination of U and Th α-emitters in NORM samples through extraction chromatography by using new and recycled UTEVA resins

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Radiochim. Acta / DOI 10.1524/ract.2012.1933

Comparison of two sequential separation methods for U and Th determination in environmental samples by alpha-particle spectrometry

By M. Lehritani[1], J. Mantero[1,*], N. Casacuberta[2], P. Masqué[2] and R. García-Tenorio[1,3]

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THANK YOU!

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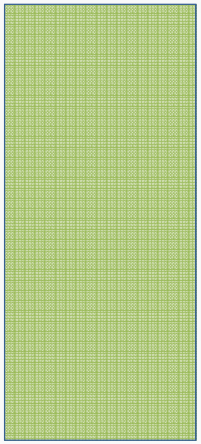

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