Gross-alpha in water

ISO-norm or Eichrom method ?

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rivm

Eichrom Users Meeting, 2005

Gross alpha or total alpha….?

- Gross alpha refers to a well described method – by definition, the result is “gross alpha”
- Total alpha : determination of all alphas in a sample
- Confusion starts in other languages, where “gross alpha” is expressed as :

  - totaal alpha (Dutch)
  - alpha globale or alpha totale (French)
  - Gesamt-alpha (total in German)
  - … total or gross (Irish ……)

Drinking Water Directive 98/83/EC

Radioactivity parameters:

Total Indicative Dose < 0,1 mSv.a^{-1}

Gross alpha < 0,1 Bq.L^{-1}

Gross beta < 1,0 Bq.L^{-1}

Tritium < 100 Bq.L^{-1}

How to determine gross alpha in drinking water reliably ?

Which “standard” method..?

Standard method (1)

- **ISO 9696** (≡ NEN 5622, in Dutch)

- Thick source method
- Evaporate aqueous sample to solid precipitate

  count a source with “infinite thickness” for alpha’s
  in practice > 200 g/m^2 or 20 mg/cm^2

  alpha’s at surface ~ alpha’s in precipitate

+ any sample can be counted
- very low efficiency (2.5 – 3 %)
- influence of humidity, and careful preparation of precipitate
- time consuming

Standard method (2)

7.1 Solids content in the sample containing the alpha emitter produces significant losses in sample counting rates of about 10 to 15 % loss at 1 mg/cm^2. Liquid samples shall be evaporated to dryness onto dishes that allow the sample to be counted directly by the detector. Solids on the dish shall remain constant in amount between related test samples, and should duplicate the density of the solids of the plated standard.

- **ASTM**
- This m

all transfers with HNO_3(1 + 30). Choose the sample size with consideration for the absorption of alpha particles in the residual solids. The size should be such that the density of the deposit on the plate shall not exceed 5 mg/cm^2.

comparative data. After drying, heat the dish to dull redness for a few seconds using a burner. Cool hygroscopic solids in a dry atmosphere and store in a desiccator until the start of counting.

Standard method (3)

- **mass attenuation curve**
- German Messanleitungen Gesamt-alpha OWASS-01-01
  + US-DOE RP710
  + NF M60 801
- Evaporation + glowing at ~ 450 ^{o}C
  determine efficiency from a mass/efficiency curve

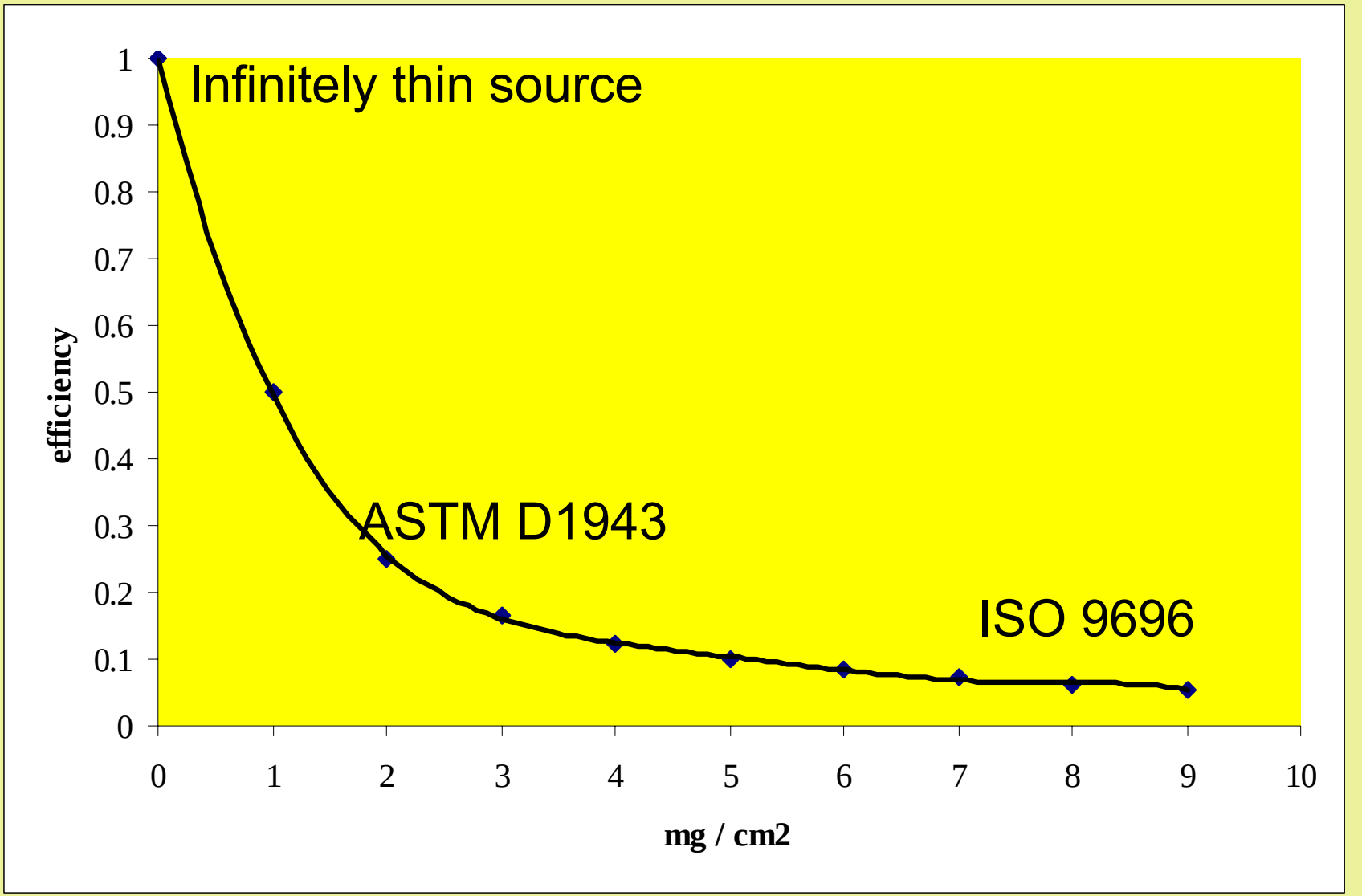
+ Large application range

- Hygroscopic salts attract moisture (also for ASTM D1943)

- Low mass » large uncertainty in efficiency

- Volatile radioisotopes of Po are (partially) lost

Mass versus efficiency curve (approx. ~ 1/x)



“Standard” method (4)

- ..the French: ISO 9696..?
- Nice norm! But we are not going to use it

- Standard-addition method…
- Add ^{241}Am spike to sample and evaporate
  compare result to sample without ^{241}Am spike

+ Intrinsic correction for mass of precipitate

- All other evaporation disadvantages

Problems with all evaporation techniques…

- If planchet is not perfectly horizontal, then evaporation will lead to precipitates or crystals at edge of planchet

  – difficult to reproduce » large sample to sample differences

- Large calibration uncertainties : > 20-30 %
- Alpha counting efficiency low and “sensitive” to external factors

- *And now for something completely different….*

Eichrom Actinide resin + LSC …?

- Resin extracts analyte out of water sample
- Alpha LSC counting efficiency ~ 100%

- No evaporation troubles and high efficiency !

- Very promising, but……

Adjusting Eichrom method (ACW 11)

- …on our lab with our equipment…
- Small problem with quantitative transfer of resin
- 55 mm filter fits well in LSC vial
- Magnetic stirring…? ⇨ “Shaken, not stirred…”

LSC optimization

- 15 ml UG-LLT + 5 ml 0.1 M HCl + filter + resin
  (Eichrom : UG-AB + resin)
- PDD setting 124 (Packard 2700 TR)
- reproducible counting conditions

Equipment

100 ml sample

300 mg resin

55 mm filter

4 hours stirring / shaking

…or overnight

LSC vials

- Stirring : filters+resin in cocktail
  filters transparant..!
- Shaking : resin in cocktail
- resin on bottom
  no negative effect !

Analytical data

- recovery of ^{241}Am 100.7 ± 1.3 % (n=20)
- alpha counting efficiency 98.6 %
- counting time 4 hours
- detection limit 0.03 $Bq.l^{-1}$ (sample size 100 ml)

OPRI drinking water intercomparison :
68 SH 300 (dec 2001)

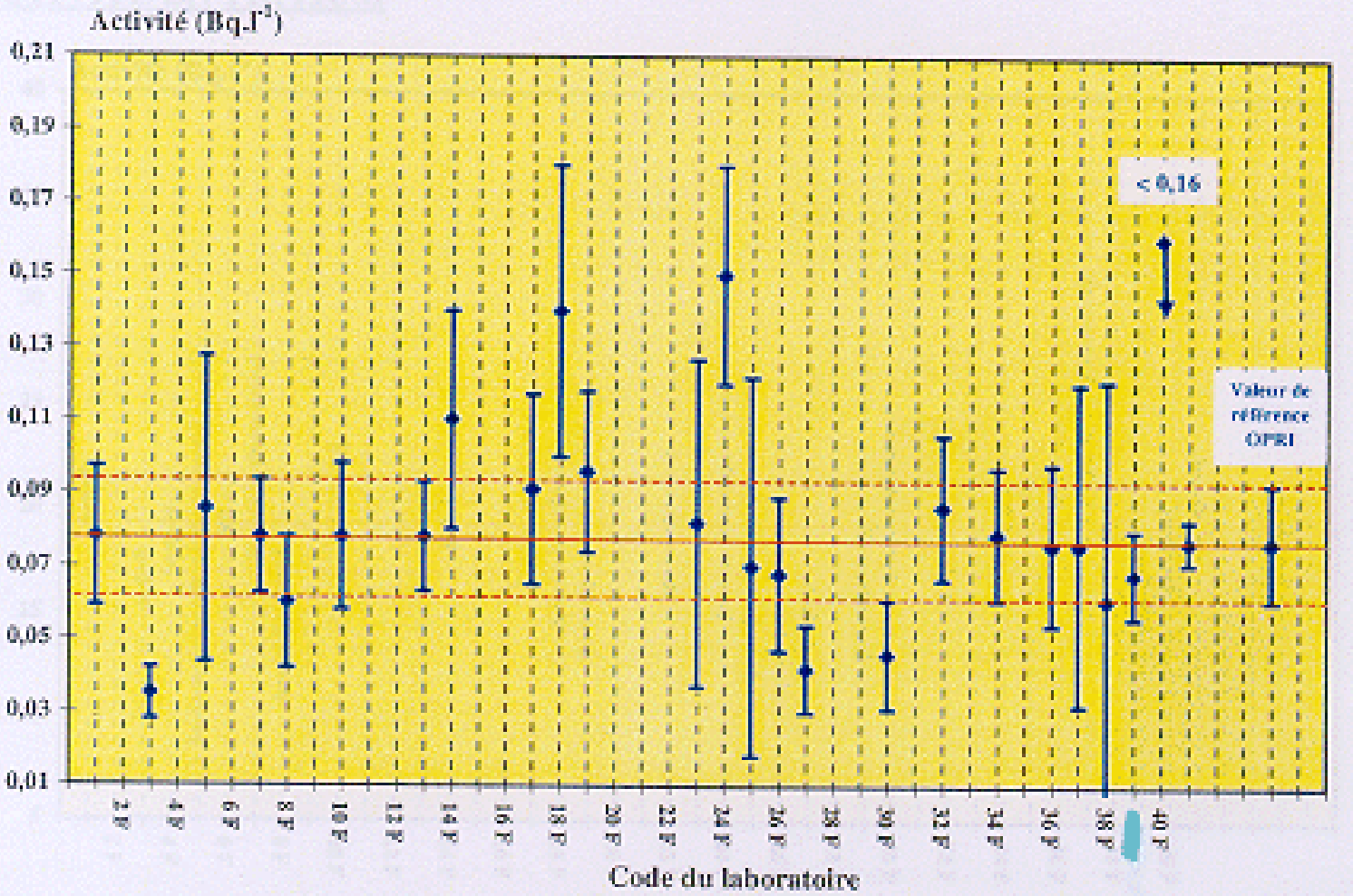
- target value : 0.077 ± 0.016 $Bq.l^{-1}$ (2s)
- reported value : 0.068 ± 0.012 $Bq.l^{-1}$ (2s)

OPRI inter-comparison 2001

INTERCOMPARAISON OPRI – 2001
Echantillon N° 68 SH 300

PRESENTATION GRAPHIQUE DES RESULTATS

ACTIVITE ALPHA GLOBALE



Conclusions :
determination of “gross alpha” using Actinide resin

- Detection limit of < 0,04 Bq/l easily achievable
  - no beta’s present on resin (such as $^{40}K^{+}$ and $^{137}Cs^{+}$)
- Method is simple : shake/stir – filter - count
  fast introduction on drinking water laboratory
- Actinide resin works very well

  - recent improvements on Ra adsorption
  (MnO_2-resin, S. Happel, Eichrom workshop, Dusseldorf, sept-’05)

- Is analytical result ≡ gross alpha ?
  Further validation and comparison with traditional techniques
- **…..but it isn’t a standard method…!**

Then we *make* it a standard method….!

ISO/IEC TC /SC N

Date: 2005-09-5

ISO-IEC_

ISO/IEC TC /SC /WG

Secretariat:

ISO Draft 2005

Determination of the gross-alpha activity concentration of samples

aqueous

S. Happel, P.Letessier, P. Kwakman

Élément introductif — Élément central — Élément complémentaire

Overview of all discussed techniques

Method	Principle	Calibration	Detection	Efficiency (approximated)	Repeatability of efficiency	Measured quantity	Waste
ISO 9696	Thick source	Spiked powder	Gas flow counting	2,5 – 3 %	-	Gross alpha	None
ASTM D1943	evaporation	Thin deposit	or scintillation	15-25 %	--	Alpha activity	None
DOE	Evaporation	Mass – efficiency curve		10-25 %	--	Gross alpha	None
Standard addition	Evaporation	Addition of standard to sample		10-20 %	--	Gross alpha	Spiked samples
Actinide resin	extraction	LSC alpha-beta discrimination	LSC	95-100 %	++	Gross Actinide equivalent activity (??)	LSC cocktail

Detection limit of 0,04 $Bq.l^{-1}$ can be achieved by all techniques

ISO norm or Eichrom method…?

- ISO and others norms lead to ‘consensus’ result not necessarily the best or most accurate
- Actinide resin is more reliable and more accurate
- LSC equipment and knowledge necessary…
- Standard methods : gross alpha screening
- Gross alpha ???

Quote of the day…..from DOE RP710

Gross screening analyses are not expected to be as accurate nor as precise as more detailed radiochemical separations. Rather, they are intended to provide rapid information associated with a particular action level with minimal chemical preparation. Additionally, these types of analyses are not intended to give "absolute" activity measurements, but rather "order-of-magnitude" estimates.

Actinide resin gives better result

higher quality has its price…

Thank you for your attention…

Extending method to nuclear waste water

- other alpha emitters than ^{241}Am
- (a lot of) beta's present in sample
- dirty samples and quench…

Case study: URENCO waste water

- containing uranium isotopes

Alpha energies of U and ^{241}Am

^{238}U 4.2 MeV alpha

- ^{234}Th 188 keV beta (24.1 d)
- ^{234m}Pa 2280 keV beta (1.17 min)

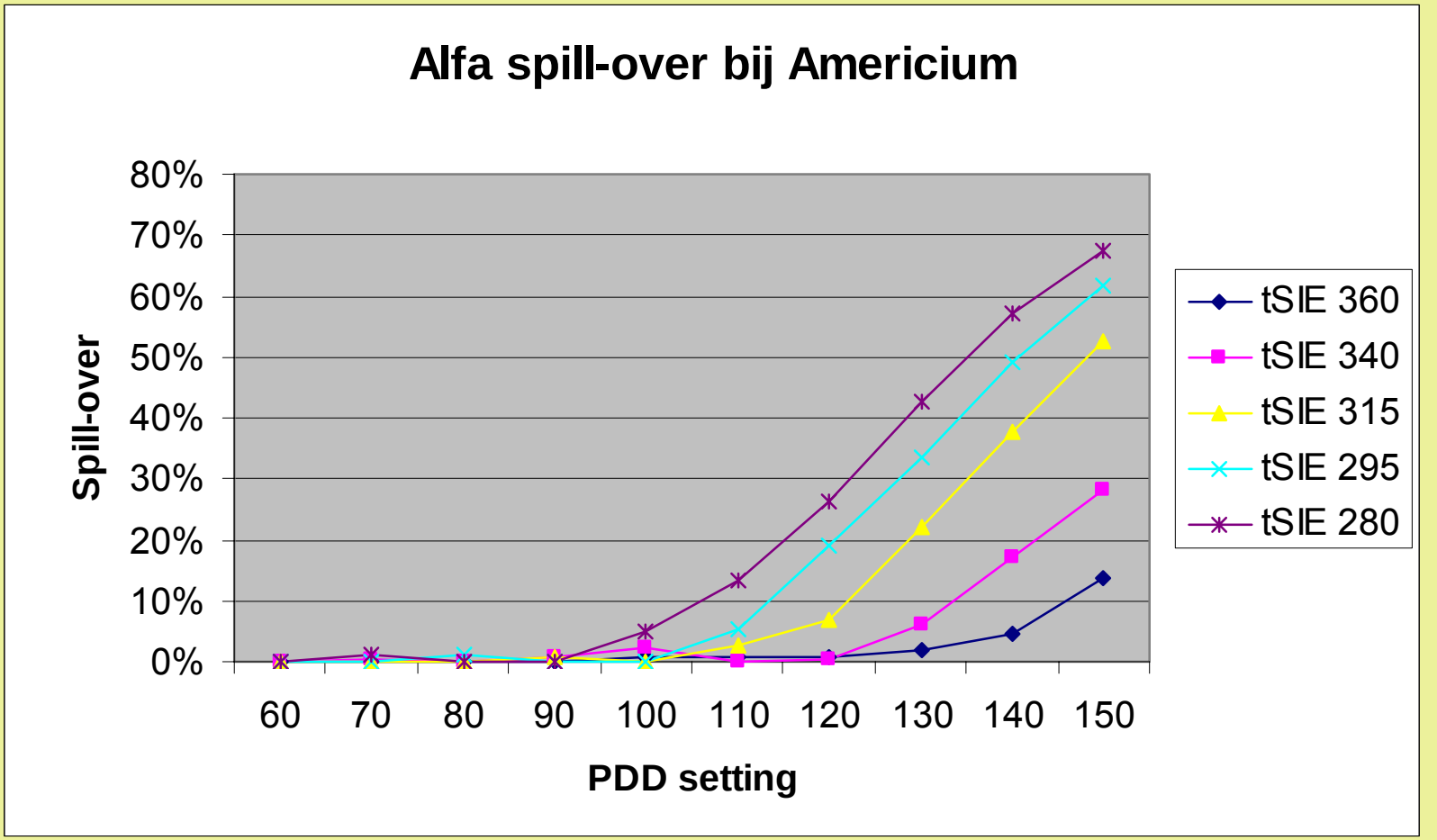
^{234}U 4.7 MeV alpha

^{241}Am 5.5 MeV alpha

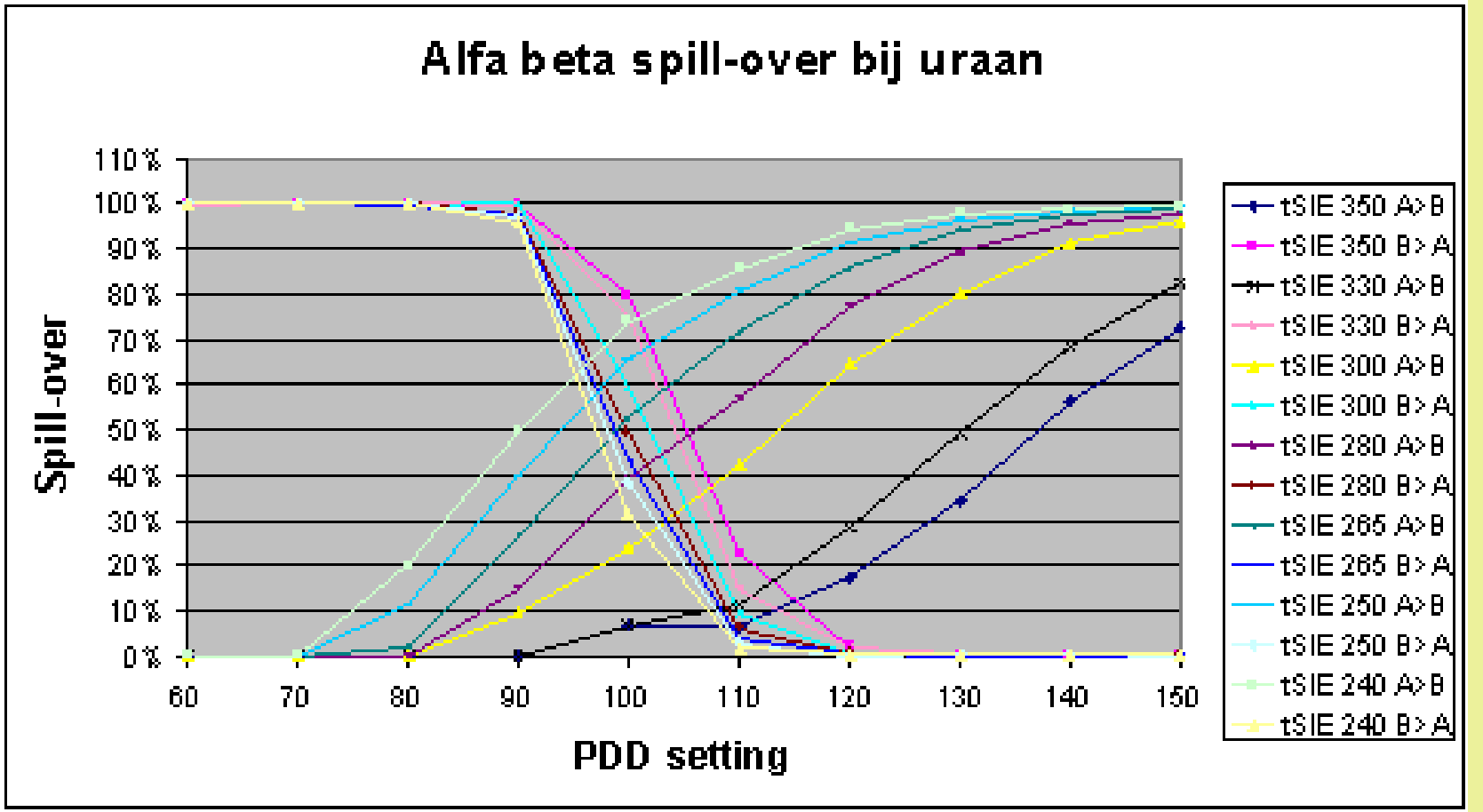
LSC discriminator setting is optimized with ^{241}Am and ^{36}Cl (709 keV)

Is this setting valid for other nuclides..?

Alpha-beta spill-over for ^{241}Am



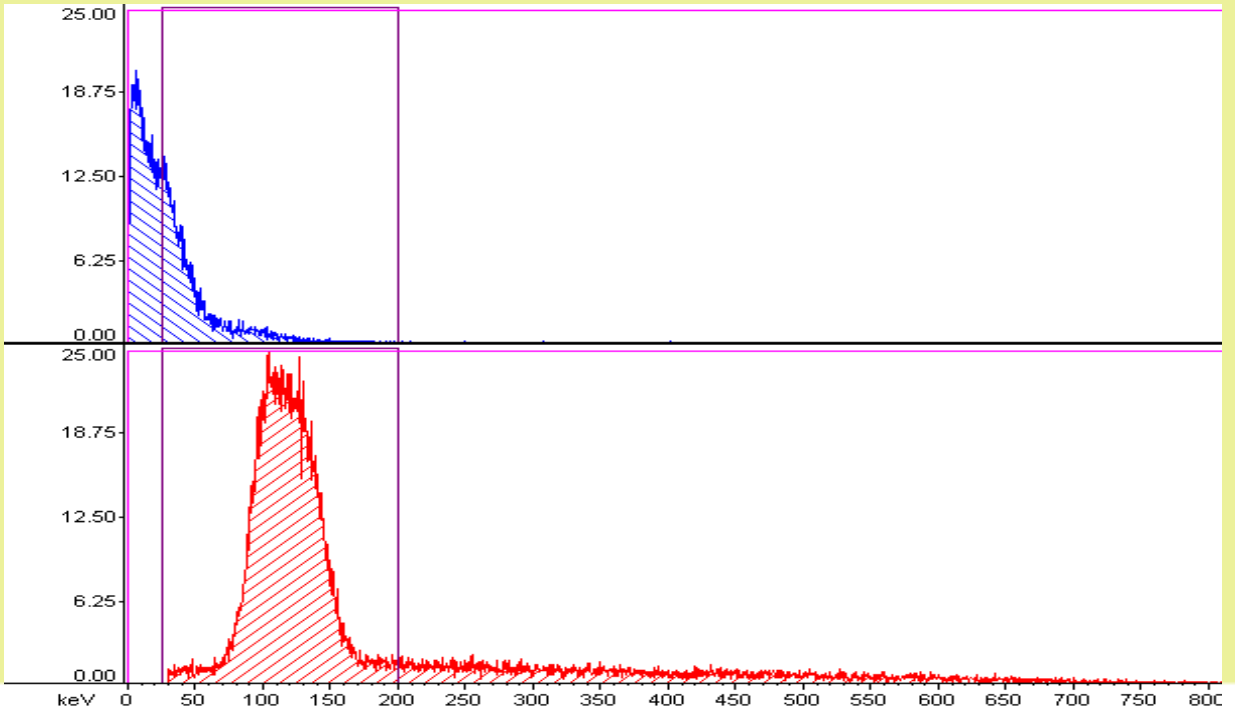
Alpha-beta spill-over for Uranium



Large influence of alpha energy and beta's

Spill-over results

- PDD setting should be > 130 to avoid beta spill in alpha spectrum
- Then the loss of alpha's may be large
- and, for Uranium, very different from ^{241}Am



Practical results in waste water

- German intercomparison Abwasser 2001 containing both ^{241}Am and Uranium

Abwasser 2001
Target value: 3.04 Bq.l^{-1}

Sample ID	PDD instelling	bruto CPM Alfa	bruto CPM beta	Spill-over alfa	Spill-over beta	netto CPM alfa	netto CPM beta	(Bq/l) alfa activiteit
AbwO1a	110	33.0	156.9	6.3%	22.8%	-0.6	190.6	-0.1
AbwO1b	110	33.7	141.5	6.3%	22.8%	3.5	171.6	0.6
AbwO1a	125	18.2	165.4	14.9%	1.2%	18.9	164.7	3.2
AbwO1b	125	17.2	150.1	14.9%	1.2%	17.9	149.4	3.0
AbwO1a	130	18.2	160.5	34.4%	0.5%	23.7	155.0	4.0
AbwO1b	130	16.5	146.6	34.4%	0.5%	21.4	141.6	3.6
AbwO1a	140	13.6	169.4	56.3%	0.2%	20.9	162.1	3.5
AbwO1b	140	13.6	155.6	56.3%	0.2%	20.9	148.3	3.5
AbwO1a	150	11.0	163.6	72.7%	0.2%	18.7	155.9	3.2
AbwO1b	150	11.0	151.0	72.7%	0.2%	18.7	143.3	3.2
						Gemiddelde:		3.4

Conclusions 2 : waste water

- method works well for alpha's in waste water
  - but also for a number of beta's as M^{2+} or M^{3+}……
- minimize beta's by shifting the discriminator setting
  - Correct for loss of alpha's
- identity of alpha emitter improves result:
  - knowing the alpha energy enables a more accurate estimation of the loss of alpha's

Conclusions 2 : waste water

- quenching has to be as low as possible
  - sample must be filtered (Eichrom procedure)
  - may result in loss of particle bound alpha-activity
- uncertainties of determination of gross alpha are much better known
- LSC knowledge needed to make it a routine method……