Nuclear Engineering Seibersdorf GmbH

Use of Cerenkov Counting for the Determination of ^{90}Sr in a Radwaste Treatment Facility

Andreas Vesely – Herbert Trombitas – Helmut Lindauer

NES as Part of AIT (Austrian Institute of Technology)

- AIT is Austria‘s largest non-university research group
- NES is a 100% affiliate of AIT with specific tasks - Austrian organization for radioactive waste management
    - Handling all radioactive waste arising in Austria (collection, processing and storage)
    - Decommissioning of former nuclear research and industrial installations

Analytical Work - Chemical and Radiological

Analysis (chemical, radiological) of different types of samples:

- Solids:
  - construction waste
  - metals/alloys
  - soil
  - ashes
  - etc.
- Liquids:
  - waste water
  - liquid waste
- Gases:
  - off-gases

Analytical Work – Standard Method for ^{90}Sr

- Leaching of solid sample with 8N nitric acid
- Addition of stable Sr as tracer (if necessary)
- Extraction chromatography with crown ether phase ("SrSpec"):
    - Subsequent elution of contaminants with 8N HNO_3 and of Sr with 0,05 N HNO_3
- Determination of Sr-recovery and purity with ion chromatography (typically 60 – 90 % recovery, high purity)
- LSC with cocktail Ultima Gold XR (sample: cocktail = 10:10 ml)

Barite-Rich Samples - An Analytical Challenge

Barite-rich samples occur frequently in decommissioning projects:

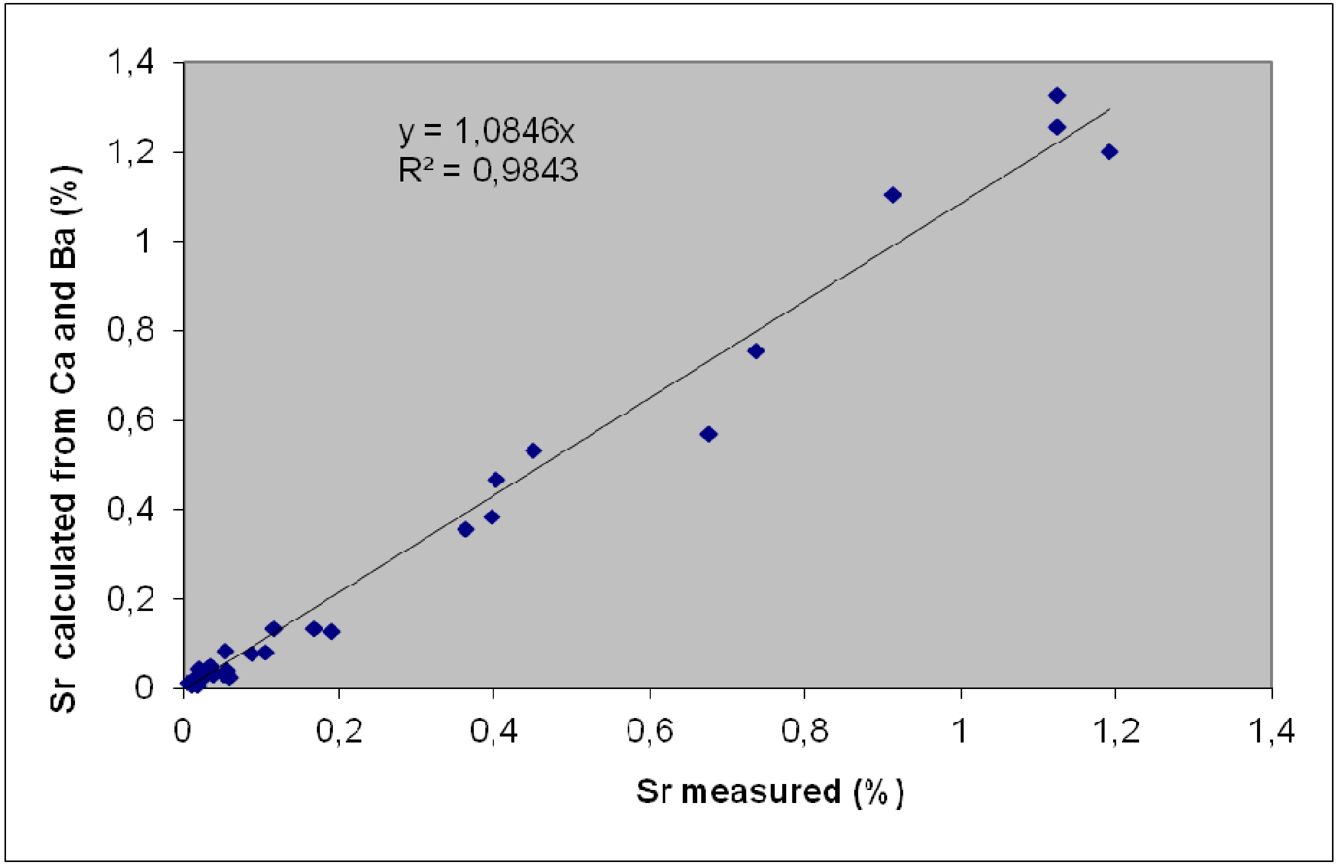
- Soil mixed with crushed concrete and barite gravel
- Shielding concrete
- Mixtures of normal and heavy concrete

Stable Sr is associated with Calcite (and materials produced from it, e. g. Portland cement) and Barite

Typical ratio (mass):

- Ca/Sr = 900 in Calcite
- Ba/Sr = 40 in Barite

Sr Associated with Calcite and Baryte



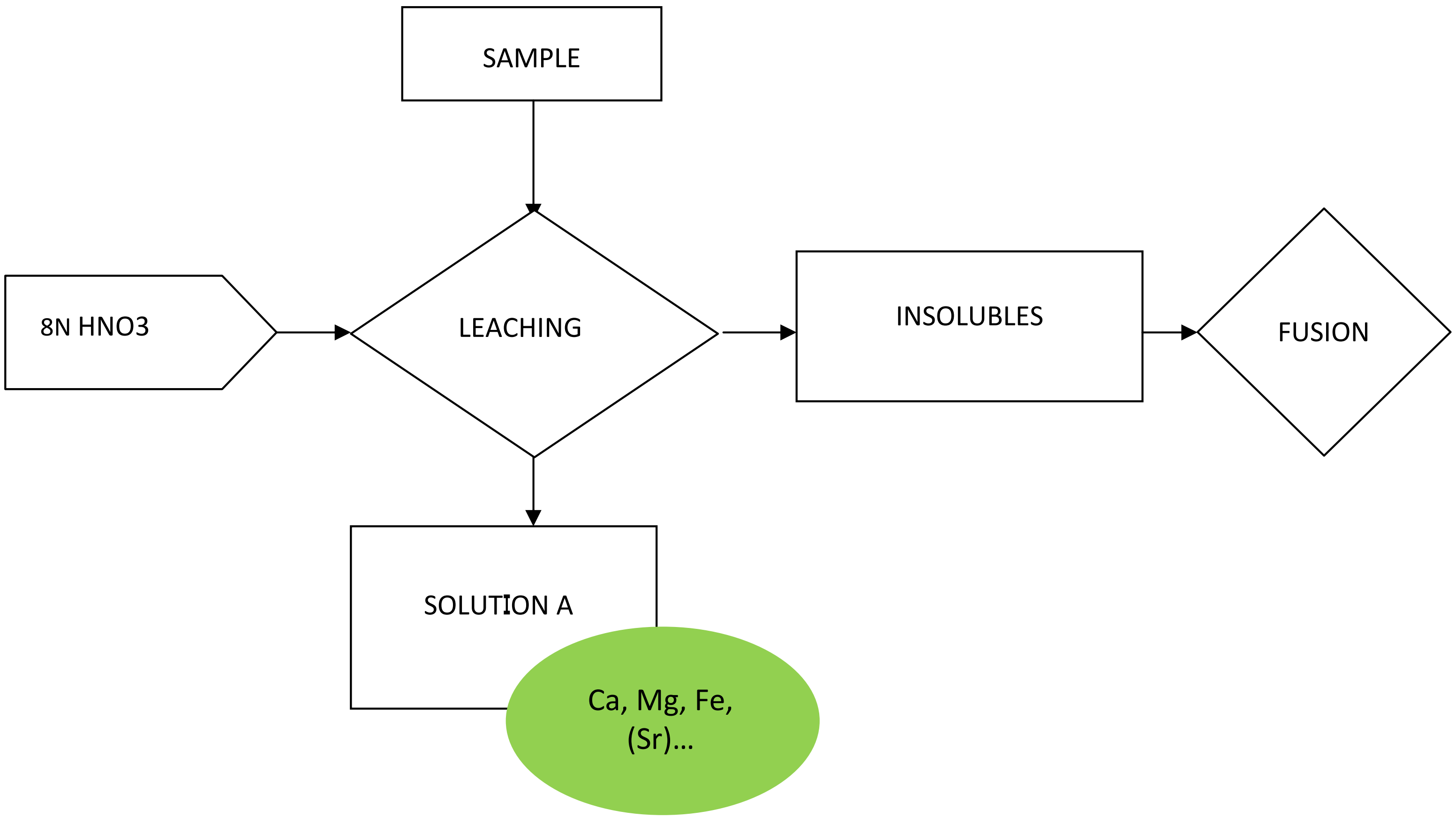
- Ca, Sr and Ba measured in various samples by XRF
- Calculation of Sr-concentrations from Ba- and Ca-concentrations and Ca/Sr- and Ba/Sr-ratios
- Good correlation of measured and calculated Sr-concentrations

Sr Associated with Calcite and Baryte

Two step dissolution process:

- Leaching with 8 N nitric acid, to dissolve the cement and calcite/dolomite fraction
- Melting of the residue with sodium carbonate to dissolve barium sulfate (and silicates)
- determination of Sr/^{90}Sr in both solutions

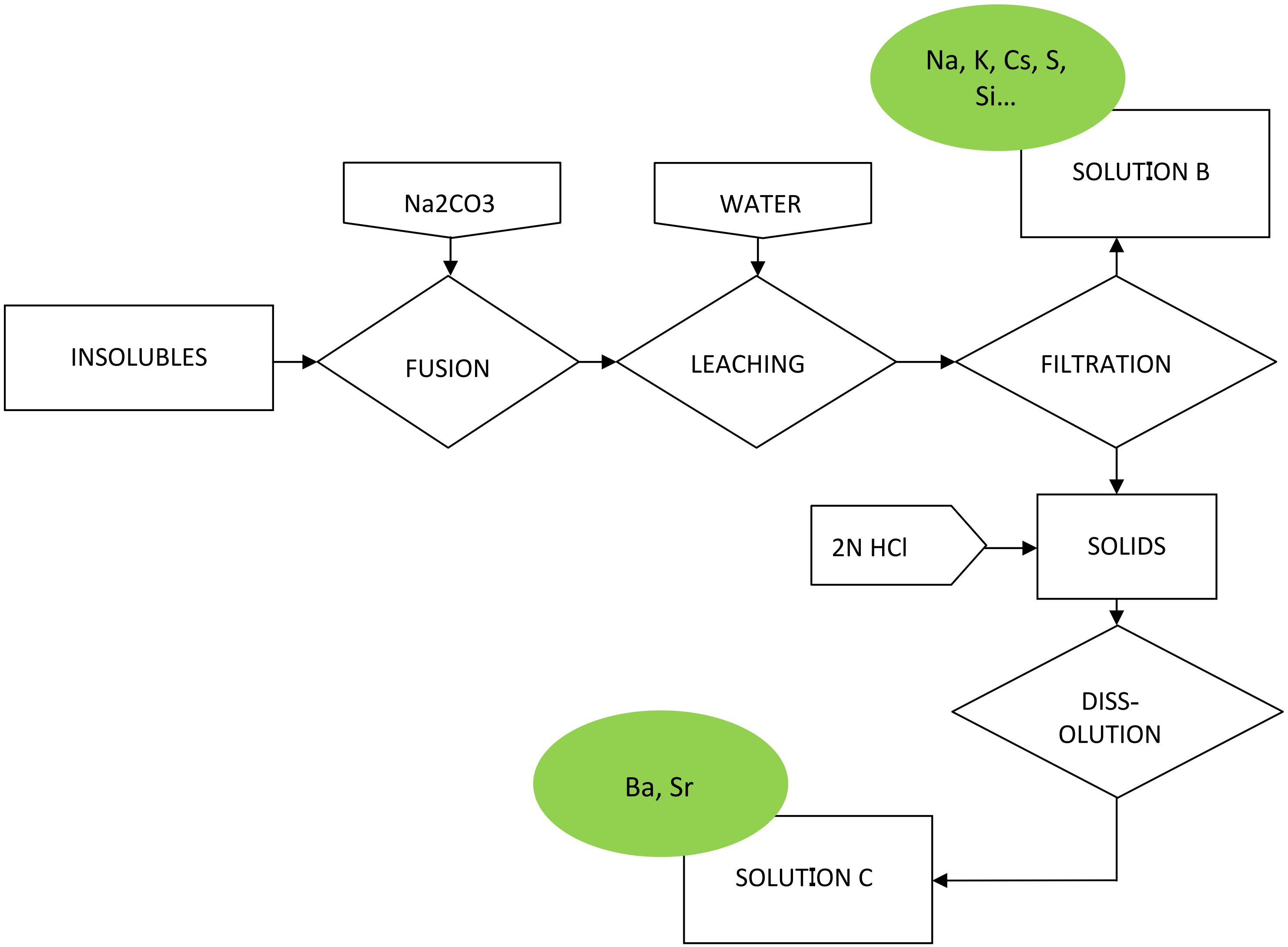
Two step dissolution process – acid digestion



Determination of ^{90}Sr in Ba-Fraction

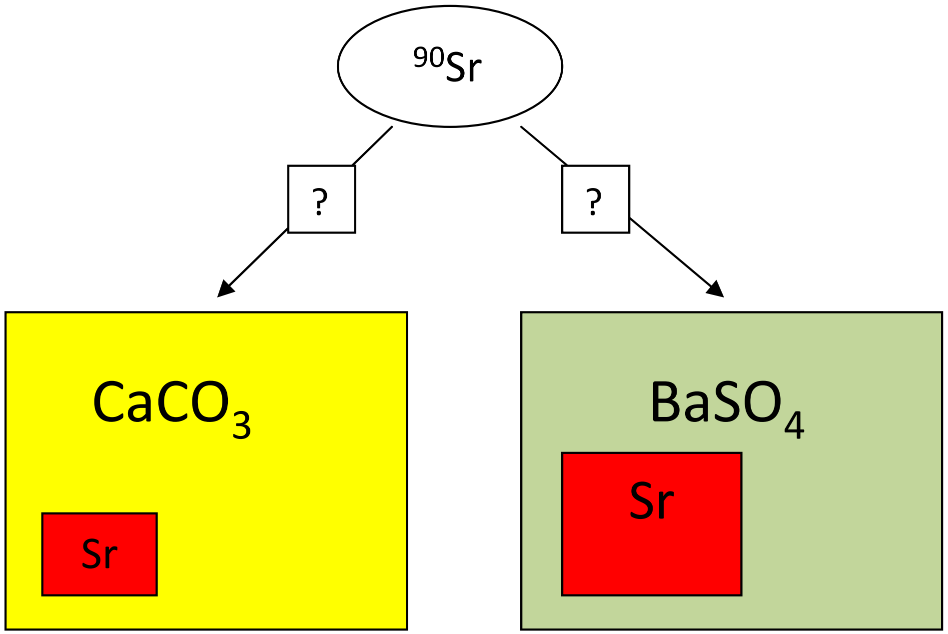
- Soda fusion process:
  - 2 – 5 g sample, fivefold amount of Na_2CO_3, melting at 1000°C for 1 h
  - Cooling of melt, leaching with hot water, filtration
  - Filtrate: excess Na_2CO_3, sulfate, silicate, <u>K,</u> <u>Cs</u>
  - Solids: Carbonates of Ca, Sr, Ba, (heavy metals) → dissolution with 2N HCl, analysis

Two step dissolution process – soda fusion



Sr Associated with Calcite and Baryte

Distribution of ^{90}Sr – like stable Sr?



Determination of ^{90}Sr in Ba-Fraction

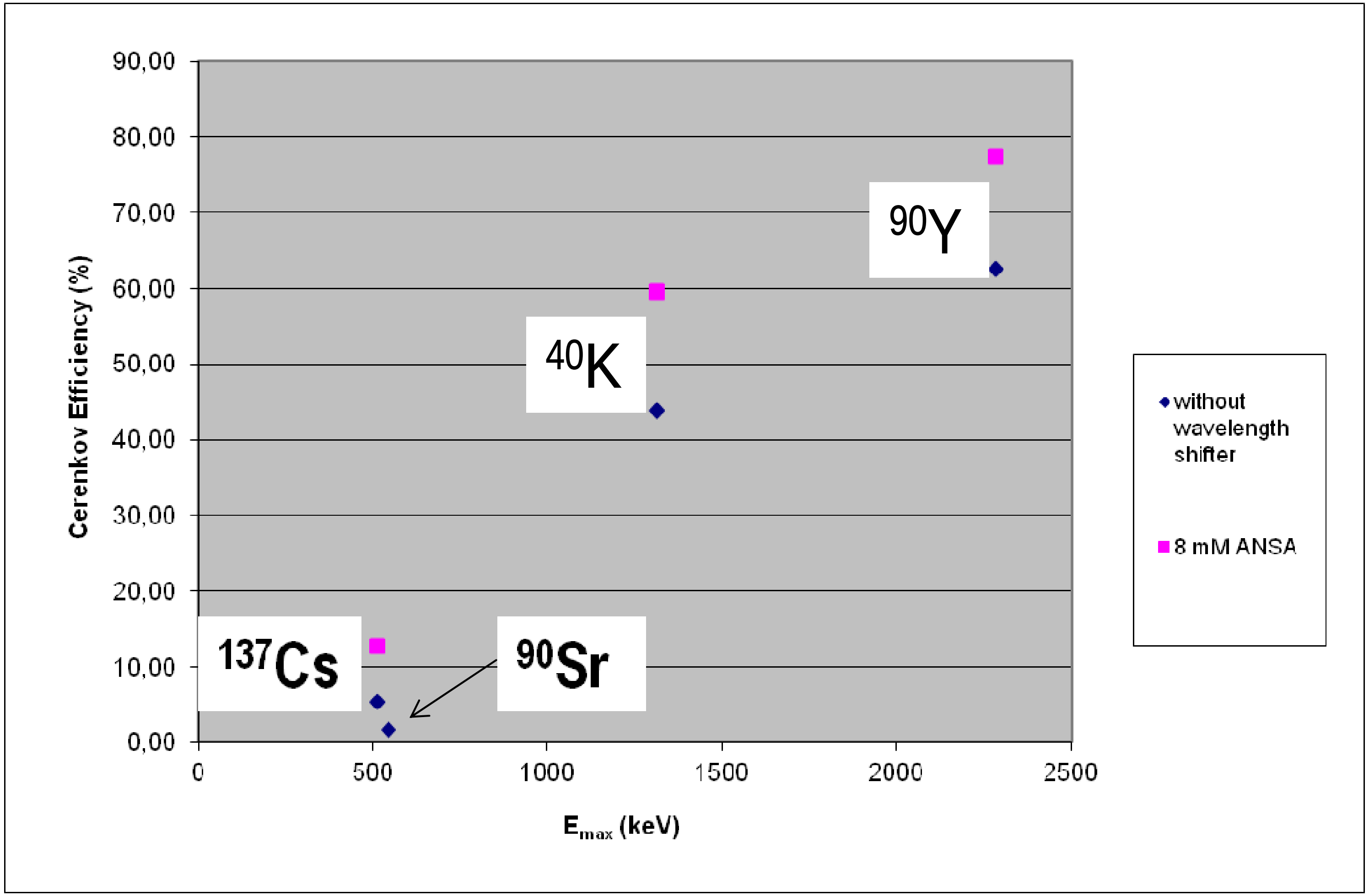
- Ba-rich solutions from soda fusion are not compatible with strong nitric acid, as required for SrSpec separation: precipitation of barium nitrate, often in gelatinous form and with time delay → clogging of chromatographic column

- Other methods:
  - Subsequent precipitation of Ba as chromate and of Sr as carbonate, LSC: good results, but labor intensive
  - Determination of ^{90}Sr by Cerenkov counting, without prior separation

Cerenkov Counting - Basic Investigations

- Measurement conditions: Perkin Elmer Quantulus, 20 ml sample, „low energy mode“, window : channels 10 - 450
- Efficiency vs. β-energy: ^{90}Sr, ^{137}Cs, ^{40}K, ^{90}Y
- Use of wavelength shifter (ANSA = 7-Amino-1,3-naphthalenedisulfonic acid, monopotassium salt)
- Color quench
- Determination of efficiency: standard addition, SQP(E), TDCR

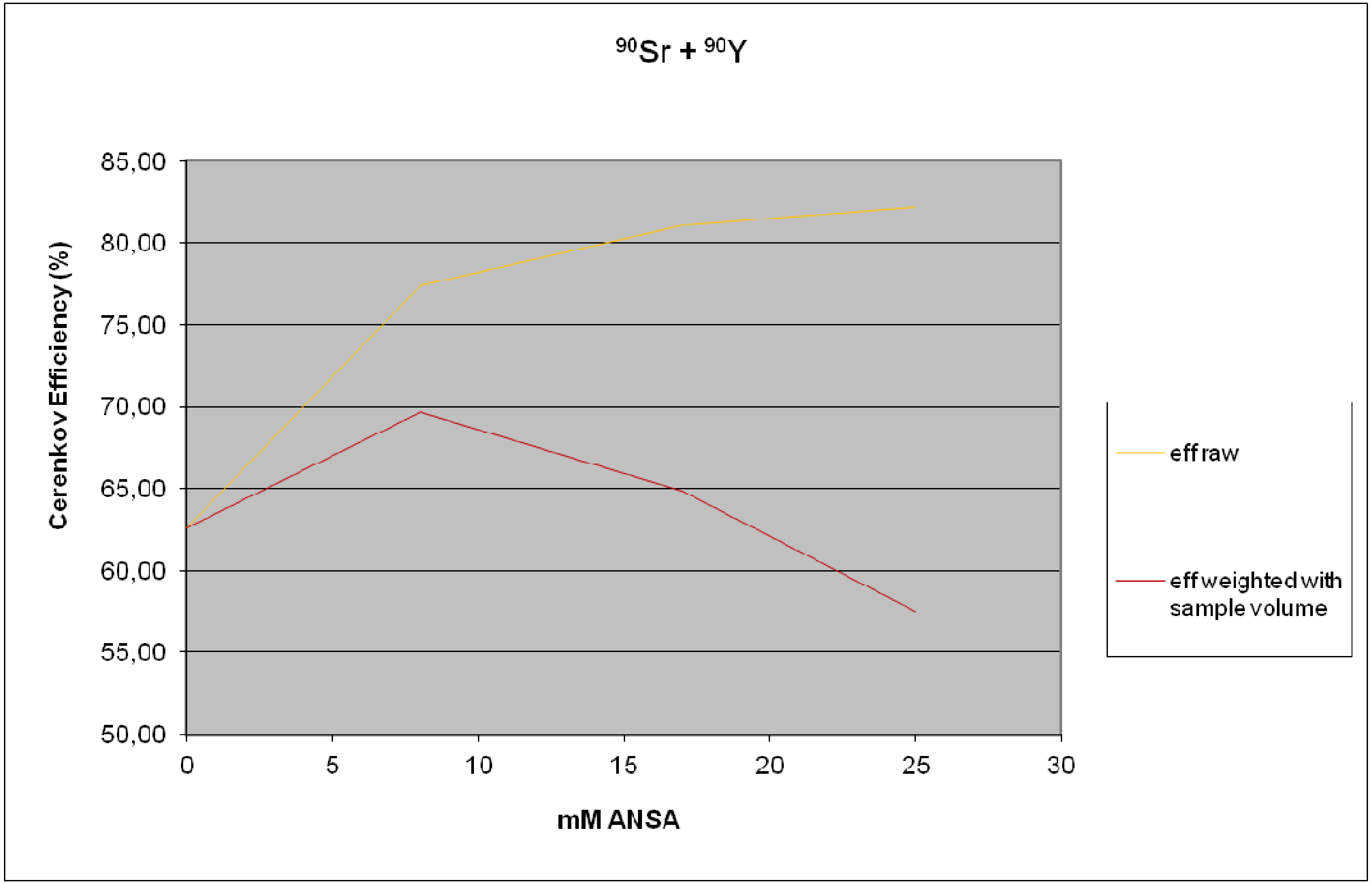
Cerenkov Counting - Efficiency vs. β-energy



Cerenkov Counting - Efficiency vs. β-energy

- Important nuclides with Cerenkov effect: $^{90}Sr/Y$, ^{40}K, ^{137}Cs, nuclides in the ^{nat}U- and Th-chain
- We measure ^{90}Y, not ^{90}Sr! Check for Sr/Y-equilibrium, repeated measurements, waiting time for ingrowth
- Enhancement with ANSA, but at higher concentrations , enhancement is counterbalanced by dilution of sample solution

Cerenkov Counting – Effect of Wavelength Shifter



Cerenkov Counting – Determination of Efficiency

- SQP(E) (irradiation with external ^{152}Eu-source) → no correlation with efficiency
- Standard addition: straightforward, but two measurements
  Addition of a small amount of standard with high specific activity (e. g. 50 mg with 200Bq ^{90}Sr/Y → insignificant change of sample color)
- TDCR: empirical correction factors for triple-to-double-coincidence-ratio necessary (e. g. 2 for ^{90}Y) → excellent results for samples with high count rate; low count rates??

Cerenkov Counting – Color Quench

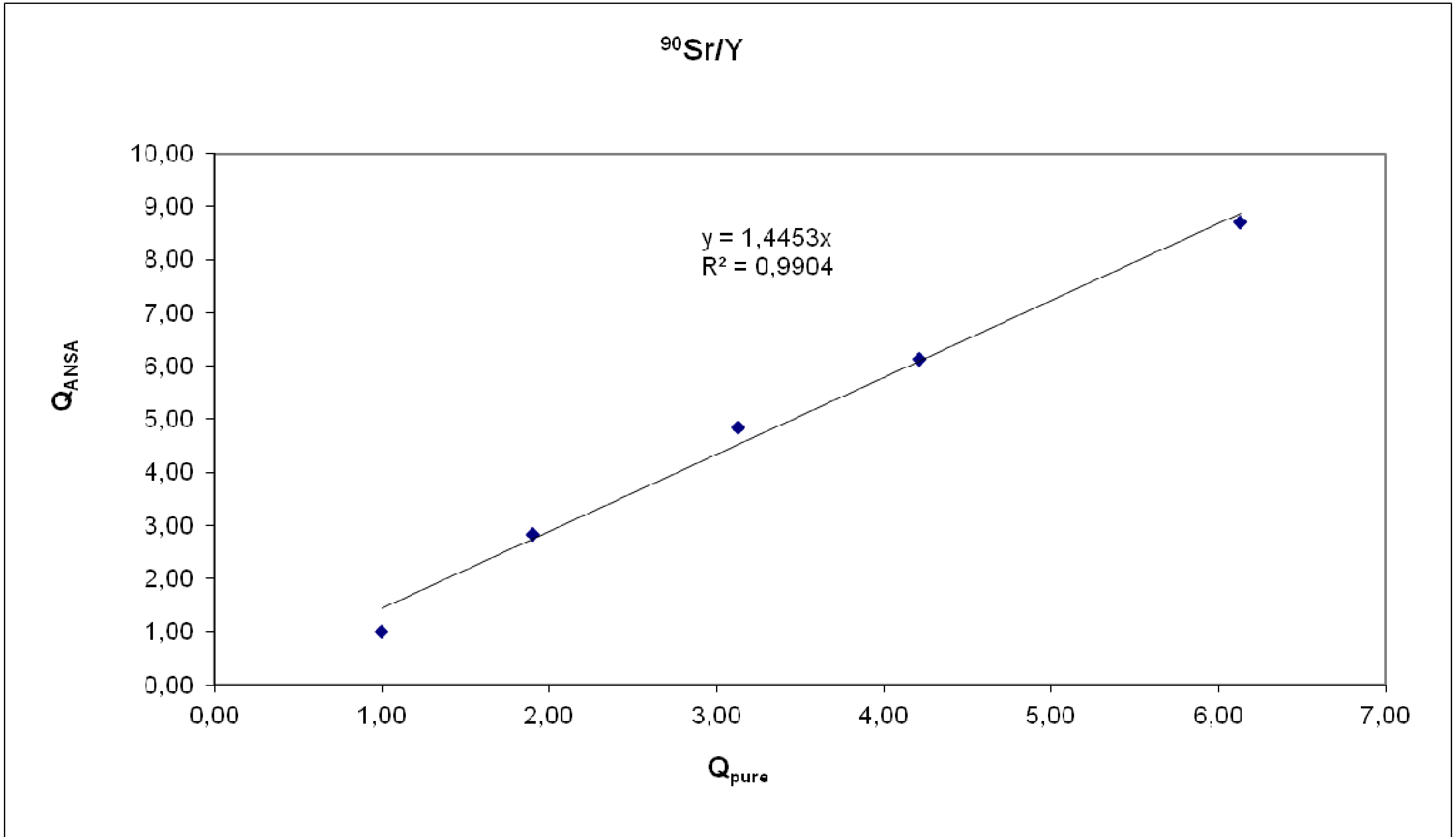
- Real samples exhibit often yellow color (Fe, Pt...) → color quench
- Definition of quench factor:

$$Q = \frac{Eff_{Standard}}{Eff_{Sample}} > 1$$

- Addition of wavelength shifter enhances quench!

  Chemical quenching is possible with wavelength shifters

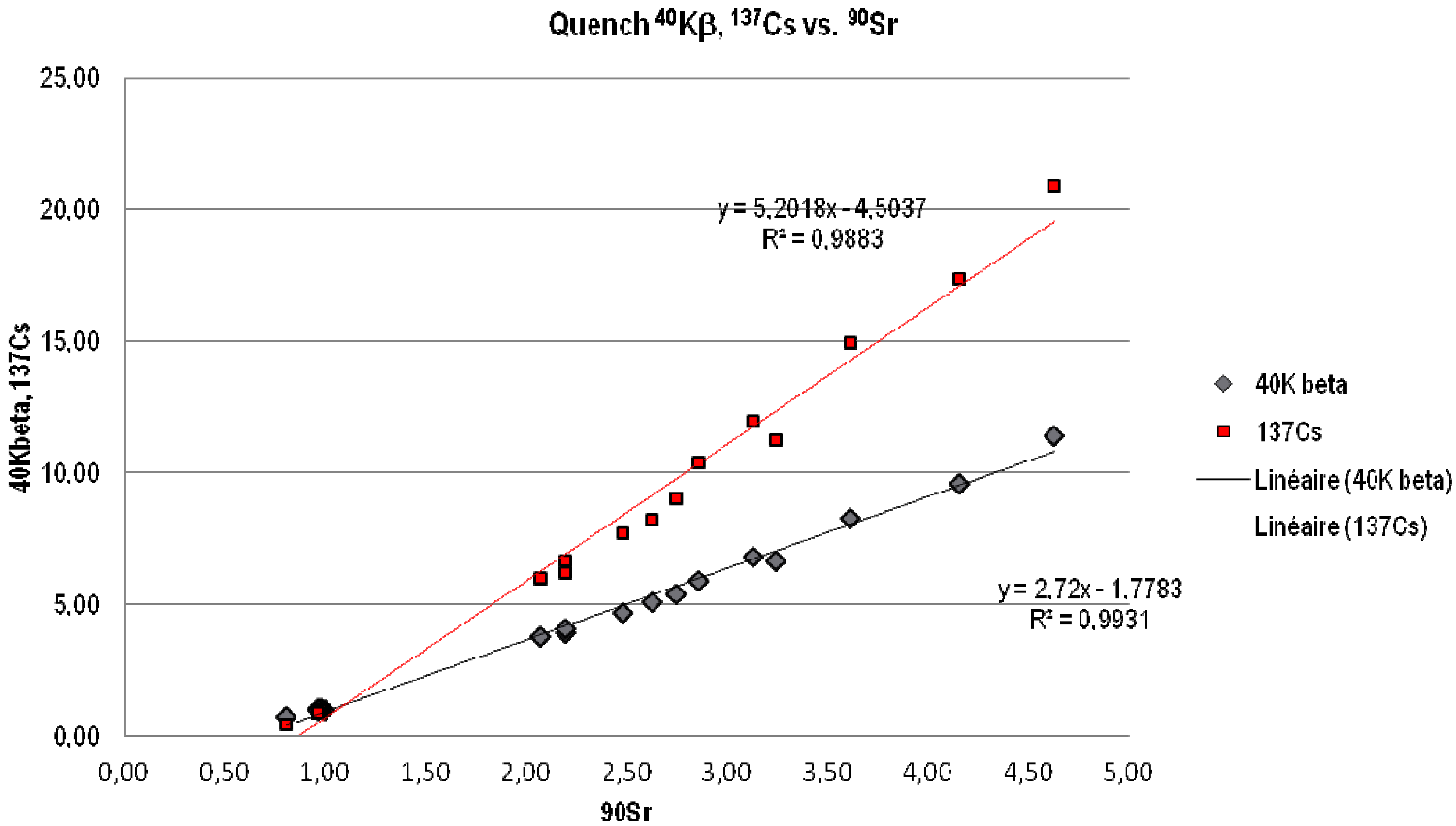
Cerenkov Counting – Effect of Wavelength Shifter on Quenched Samples



Cerenkov Counting – Color Quench

- Good correlation of Q-factors for various radionuclides → Q-factors for different radionuclides (e. g. ^{40}K, ^{137}Cs) can be calculated from the efficiency determination for one nuclide (usually ^{90}Y)
- Analysis of a sample containing ^{40}K, $^{90}Sr/Y$, ^{137}Cs:
    - Cerenkov counting, gamma spectrometry (^{137}Cs), ion chromatography (K → ^{40}K)
    - Standardaddition $^{90}Sr/Y$: determination of Q-factors for all nuclides
    - Correction of count rate for ^{40}K and ^{137}Cs
    - Calculation of $^{90}Sr/Y$-activity

Cerenkov Counting – Color Quench

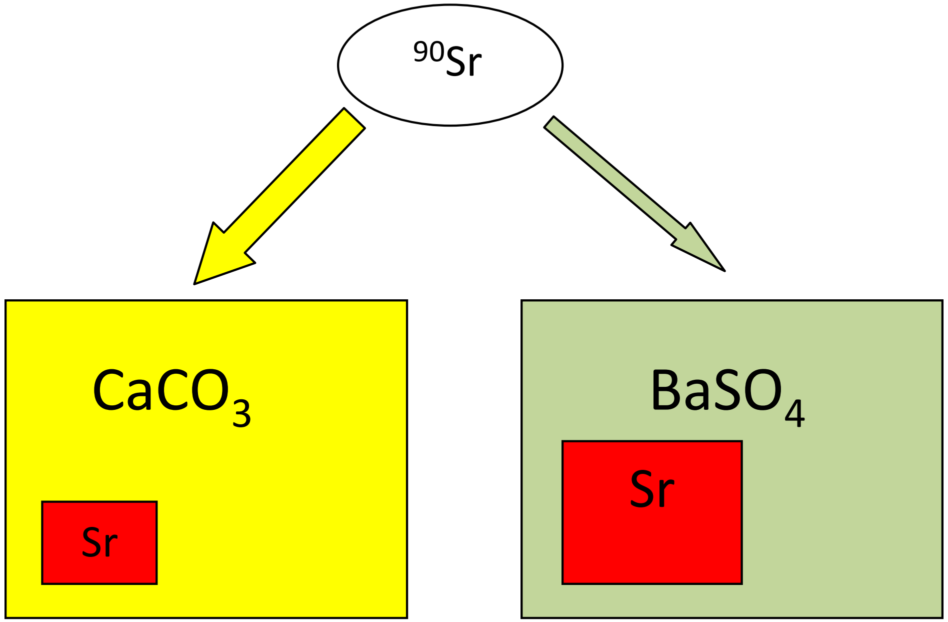


Determination of ^{90}Sr in Ba-Fraction - Results

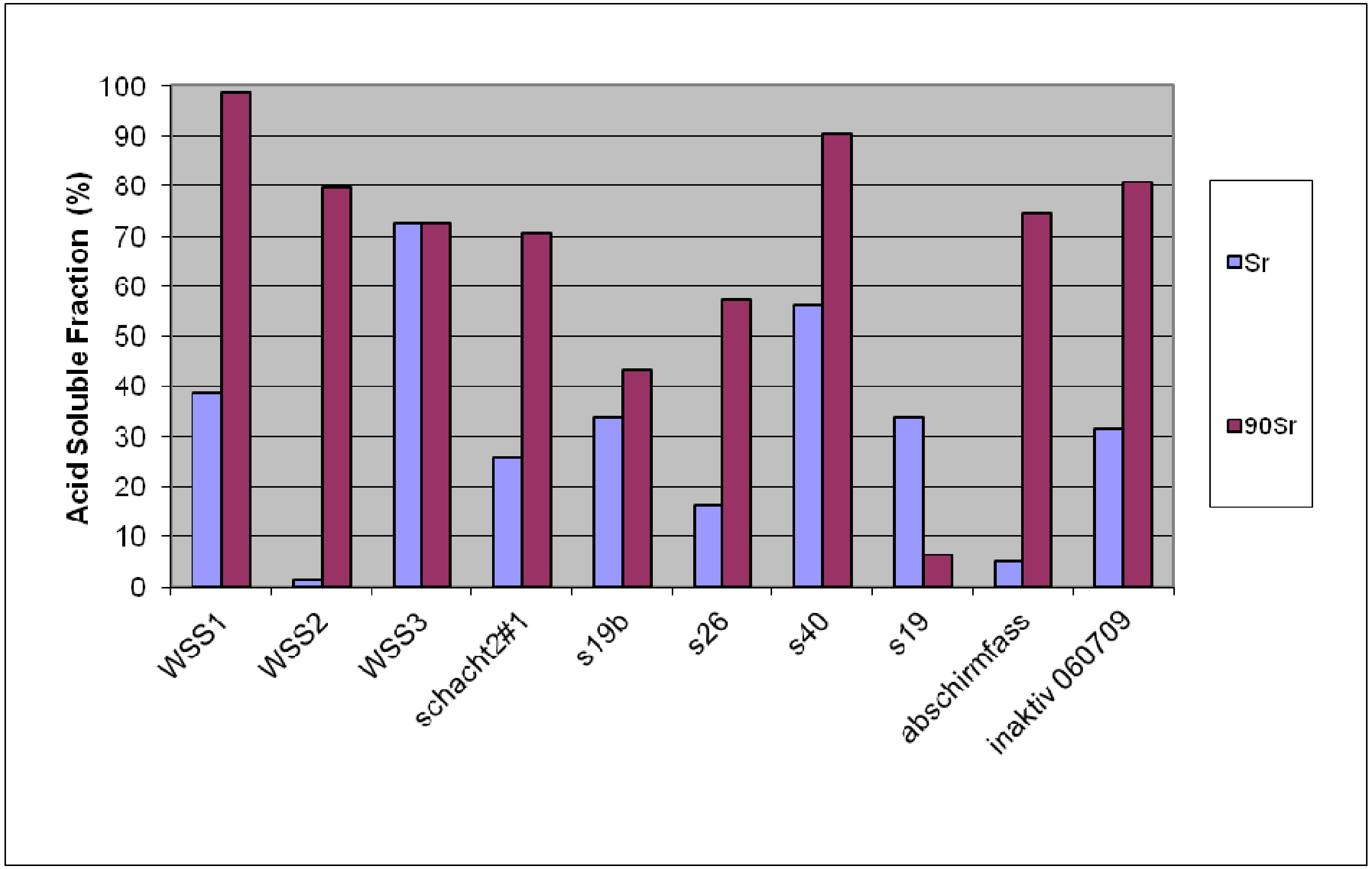
- Preparation and characterisation of a synthetic standard by precipitation Ba, Sr and ^{90}Sr with sulfuric acid (Ba/Sr=40:1, 20 Bq ^{90}Sr/g)
- Application of analytical procedure to synthetic standard, real samples and mixtures therefrom
- Recovery of Sr 80 - 100%
- Good separation of K and Cs from Sr
- Cerenkov efficiency 30 - 40 %
- Method can be applied to whole sample (without acid leaching step → reduced analytical time and effort)

Determination of ^{90}Sr in Ba-Fraction - Results

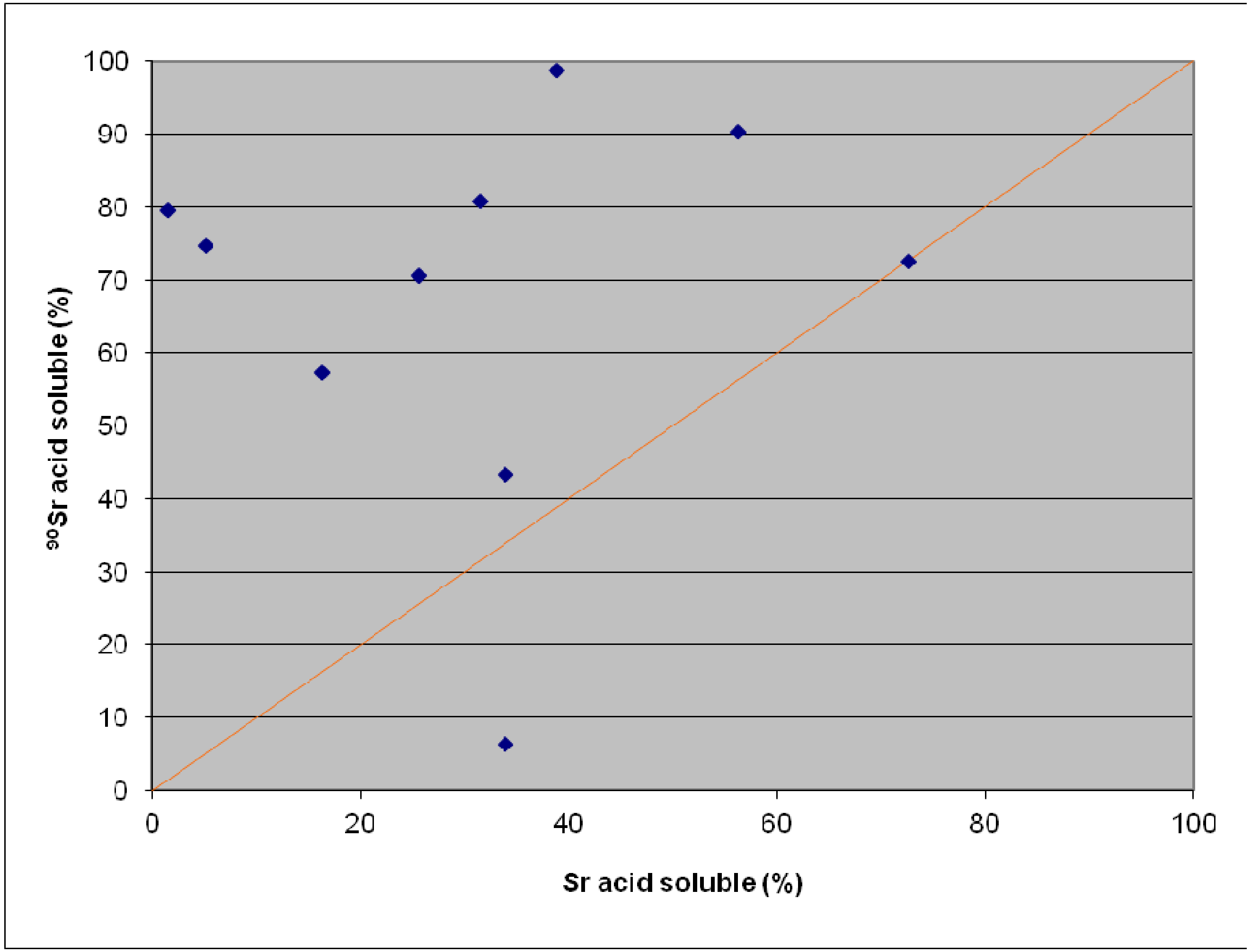
^{90}Sr (nearly) always enriched in Calcite-fraction (in contrast to stable Sr)



Determination of ^{90}Sr in Ba-Fraction - Results



Determination of ^{90}Sr in Ba-Fraction - Results

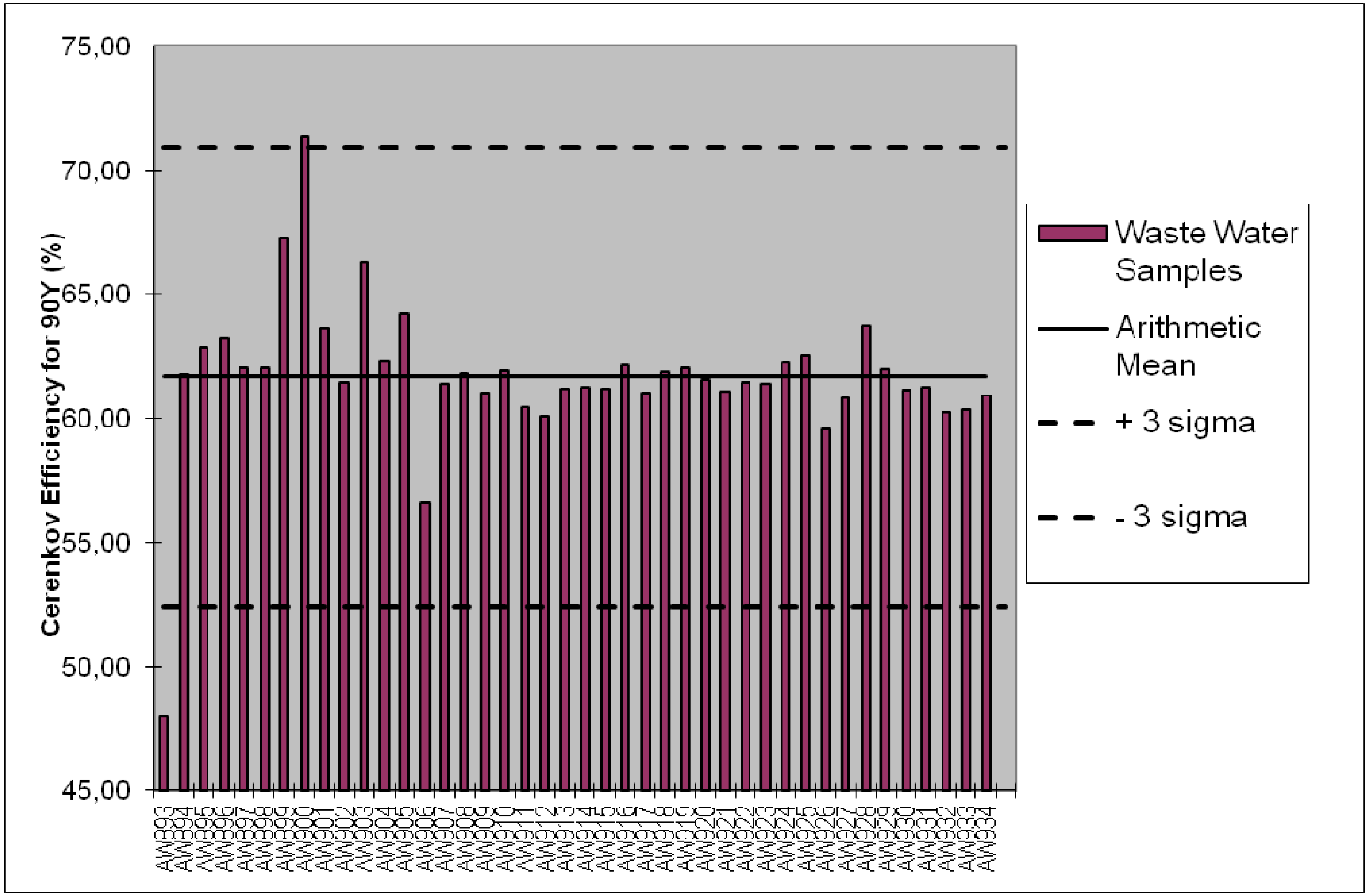


Cerenkov Counting as Screening Method for Solid Samples

		^{90}Sr (Bq/g)	
Sample Name	Type	Cerenkov	SrSpec, LSC
IWK-F 07	soil	0,19	0,21
Inakt060709	sediment from sewage system	6,30	5,95
AF VA	concrete	0,10	0,16

Cerenkov Counting as Screening Method for Waste Water

Effiency for $^{90}Sr/Y$ in waste water samples – little variation; use of mean efficiency for screening measurements



Use of Cerenkov Counting for the Determination of ^{90}Sr - Conclusions

- Cerenkov Counting is a simple and fast analysis method with fair to good sensitivity for $^{90}Sr/Y$
- Efficiency determination with standard addition (TDCR ?)
- Method applicable to barite-rich samples
- Barite/Calcite-mixtures contaminated with ^{90}Sr: ^{90}Sr enriched in Calcite-phase
- Screening method for ^{90}Sr in various types of samples (soil, concrete, waste water…)

Use of Cerenkov Counting for the Determination of ^{90}Sr - Conclusions

•Open questions: nuclides from the ^{nat}U- (^{234m}Pa, ^{214}Bi, ^{210}Bi) and Th-chain (^{228}Ac, ^{212}Bi, ^{208}Tl) have highly energetic beta-emission and are often not in equilibrium with their parent nuclides → difficult to account for (work in progress)

• Caveat: $^{90}Sr/Y$-equilibrium has to be verified