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The role of LSD spikes in safeguarding nuclear reprocessing plants

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Introduction

1. Background
2. Historical progress
3. Present status
4. Problems and future development

Basic considerations

LSD spikes are classical spikes used for measuring the isotope amount content of U and Pu in mainly spent nuclear fuel solutions by isotope dilution mass-spectrometry (IDMS)

Special features –

mg size of the spikes so that the dissolver solution does not need dilution before spiking

^{239}Pu and ^{235}U are the spikes used at present: the isotopes measured in the sample are ^{240}Pu and ^{238}U

The ^{235}U is diluted to 20% with a certified ^{nat}U material

To measure the amount of U and Pu total concentration, separate measurements of the isotopic ratios relative to the ^{240}Pu and the ^{238}U

Why these two spike isotopes?

- **Availability**

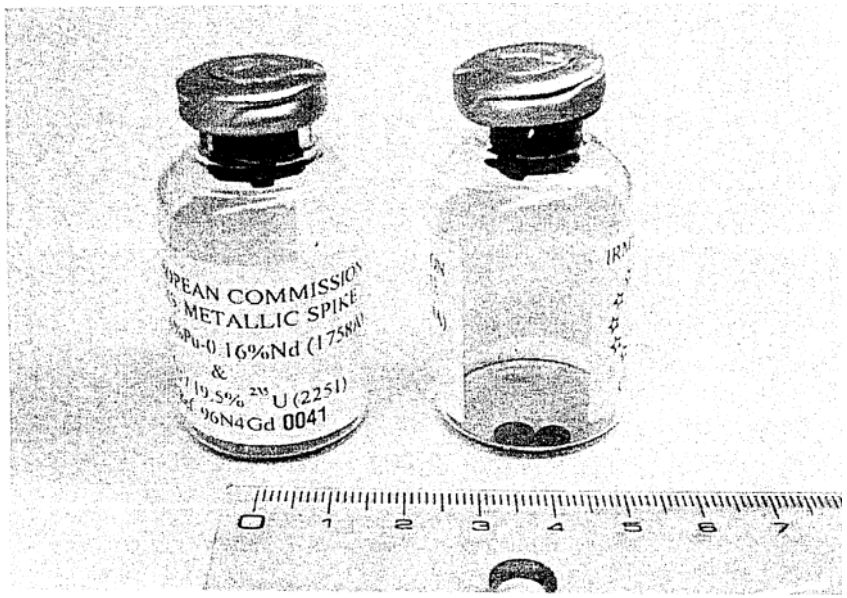
  ^{239}Pu is available as a certified metal at > 95% enrichment

  ^{235}U and ^{nat}U are available for purchase as high purity certified metals

  Other isotopes do not provide advantages or are not available easily as certified gram-sized quantities

Historical development

- **IRMM (De Bièvre) was one of the first institutes to propagate the use of LSD spikes – support program to the IAEA (1980)**
- **The first spikes proposed were metals – an 20% isotopic enriched uranium and a Pu/Gd/Nd alloy**



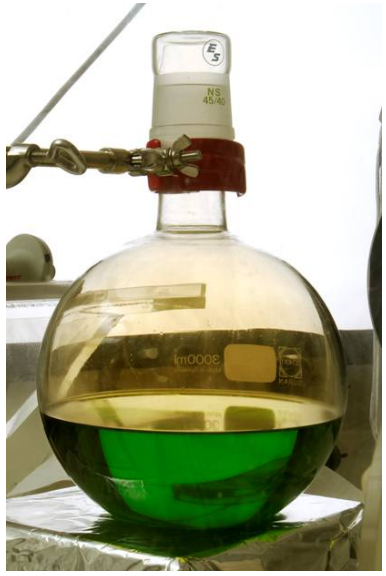
Metal spikes

Metals had advantages in handling and in the chemistry after adding the sample (reduction) but they needed specialist knowledge to make to a high standard, were difficult to prove homogeneity (Pu) and –especially for the Pu alloy – needed additional certification

Production halted at IRMM around 2000

LSD spikes at IRMM

- These are prepared by dissolving a primary ^{239}Pu metal (e.g. CETAMA MP2) and an enriched ^{235}U metal plus a natural U metal to form the needed 20% enrichment
- The materials are dissolved in ca. 3 kg 3M HNO_3 to form a homogeneous solution, ca. 0.6 mg/g ^{239}Pu and 18 mg/g U (≡ 3.7 mg/g ^{235}U)
- After drying in 2.5g batches at low temperature, a solution of cellulose acetate butyrate is added to each vial and dried down on the spike to keep it in place during storage and transport



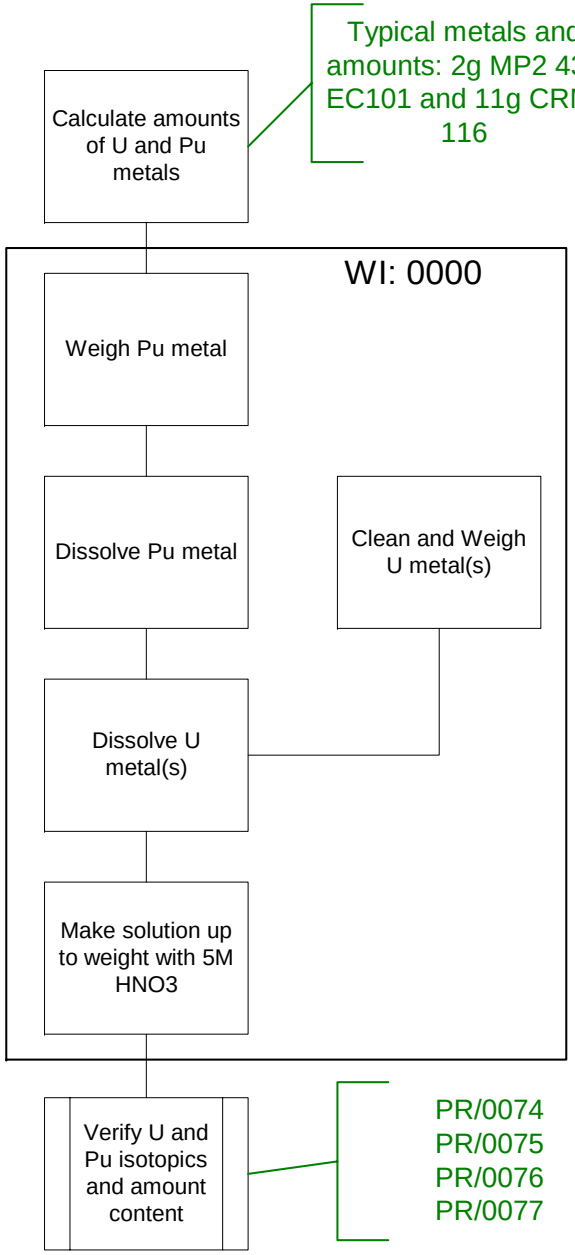
Spike amounts

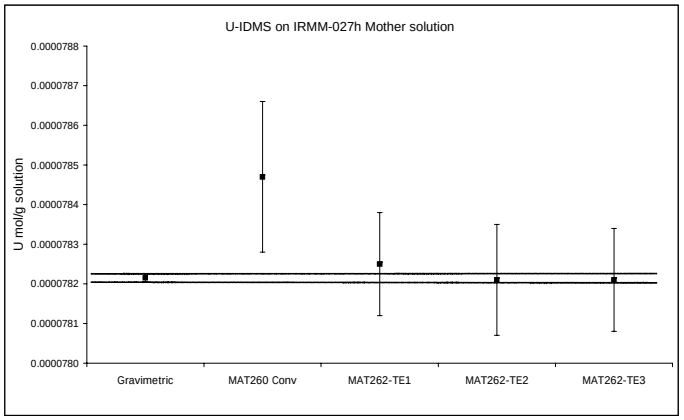
- **Uranium (20% enriched) = 18.5 mg/g solution**
  - ^{235}U = 3.6 mg/g solution = 11 mg per spike ampoule
- **Pu (> 95% enriched ^{239}Pu) = 0.6 mg/g solution**
  - ^{239}Pu = 1.5 mg per spike ampoule

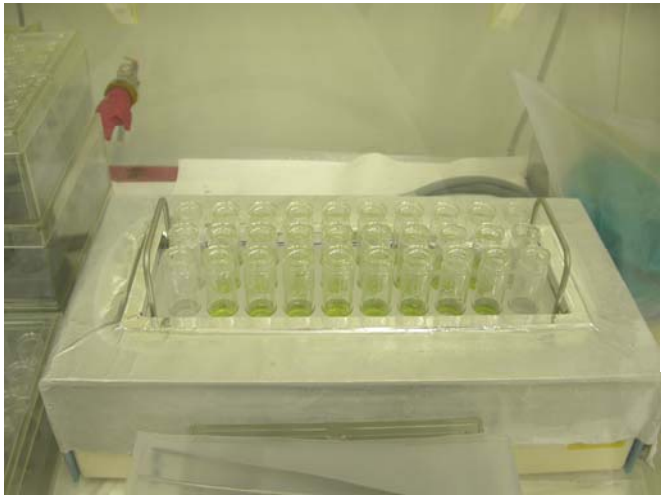
Transport and stability

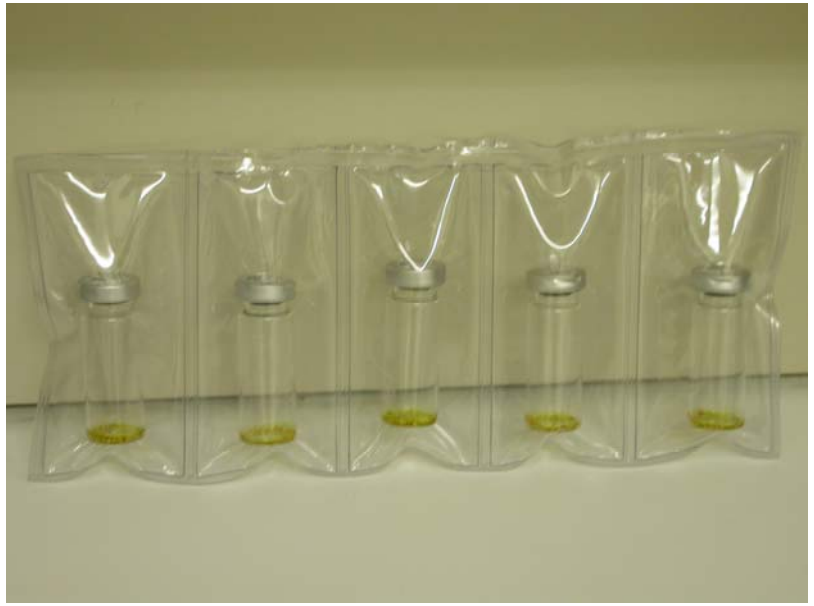
- The dried nitrates are not stable over time and tend to flake off. For this reason the first batches of the LSD spikes (1027a → 1027e) were covered with tetrahydrofuran, which was dried down onto the spike.
- This covering was very stable, but not always easy to dissolve under commercial conditions. A substitute material – cellulose acetate butyrate was chosen and is used at present

LSD spike process









verification ok?

If NO then remeasure

2nd verification ok?

If NO then stop procedure

Aliquot into vials

Dry at low temperature

Prepare 10% solution of CAB in acetone

Add organic solution and dry

Cap and seal

Verify U and Pu amount contents

PR/0074
PR/0075
PR/0076
PR/0077

Verification ok?

If NO then remeasure

Verification ok?

If NO then stop procedure

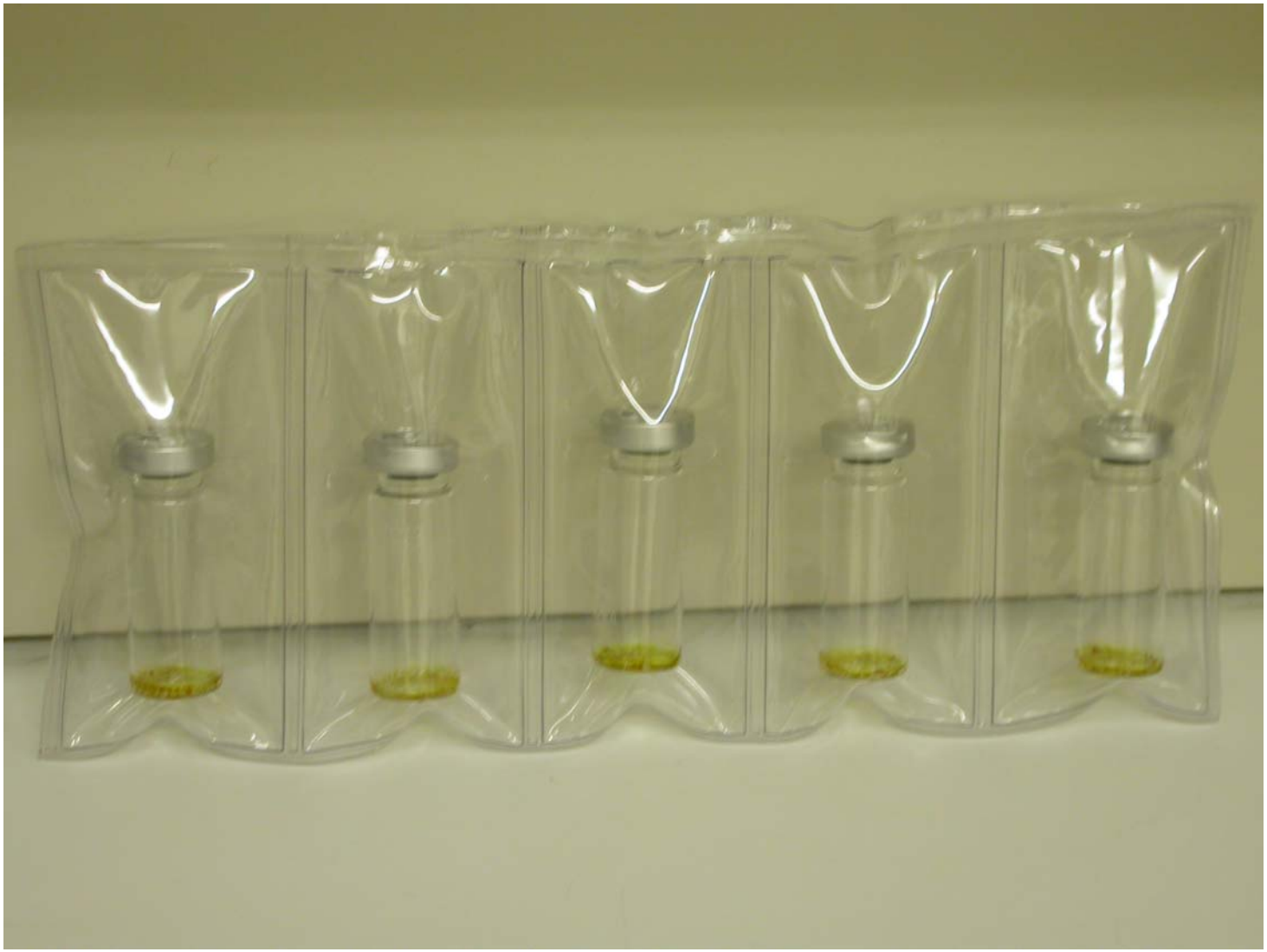
CERTIFY

Verification

Solution is verified for isotope content :

6 independent samples, spiked with e.g. IRMM-046b (^{233}U + ^{242}Pu)and separately checked for isotopic ratios: $^{238}Pu/^{239}Pu$, $^{240}Pu/^{239}Pu$, $^{241}Pu/^{239}Pu$, $^{242}Pu/^{239}Pu$; $^{234}U/^{238}U$, $^{235}U/^{238}U$, $^{236}U/^{238}U$

After ampouling, a randomly selected set across the sequence are taken and again the isotope contents are measured after spiking with IRMM-046b



Traceability

The isotope concentrations in the final LSD spike are derived from:

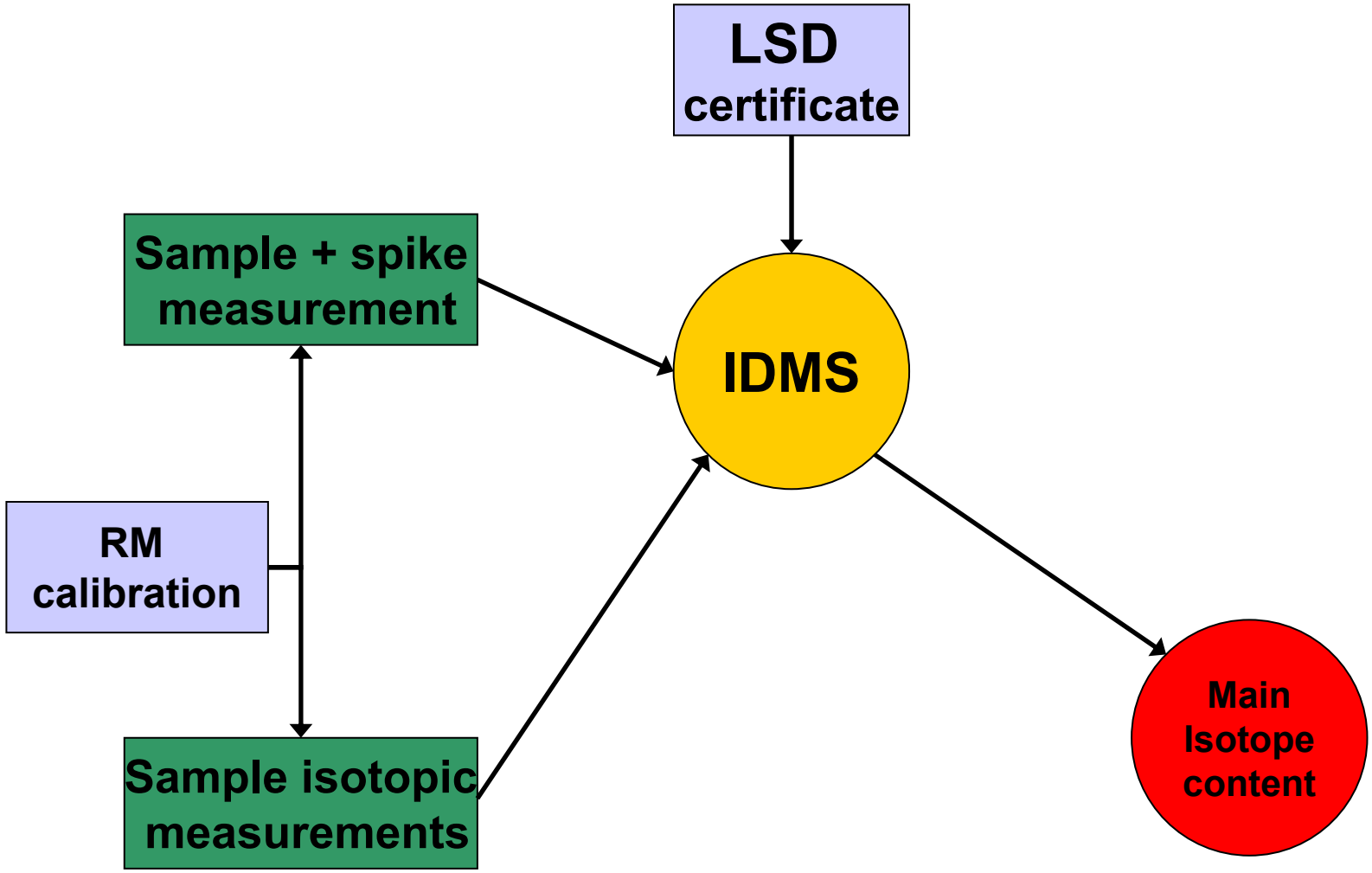
a) The weights of metals dissolved and weight of final solution

b) The certified purities of the metals

c) The certified isotopic content of the metals

This allows the direct measurement of U and Pu content in a sample by IDMS in a single traceability step

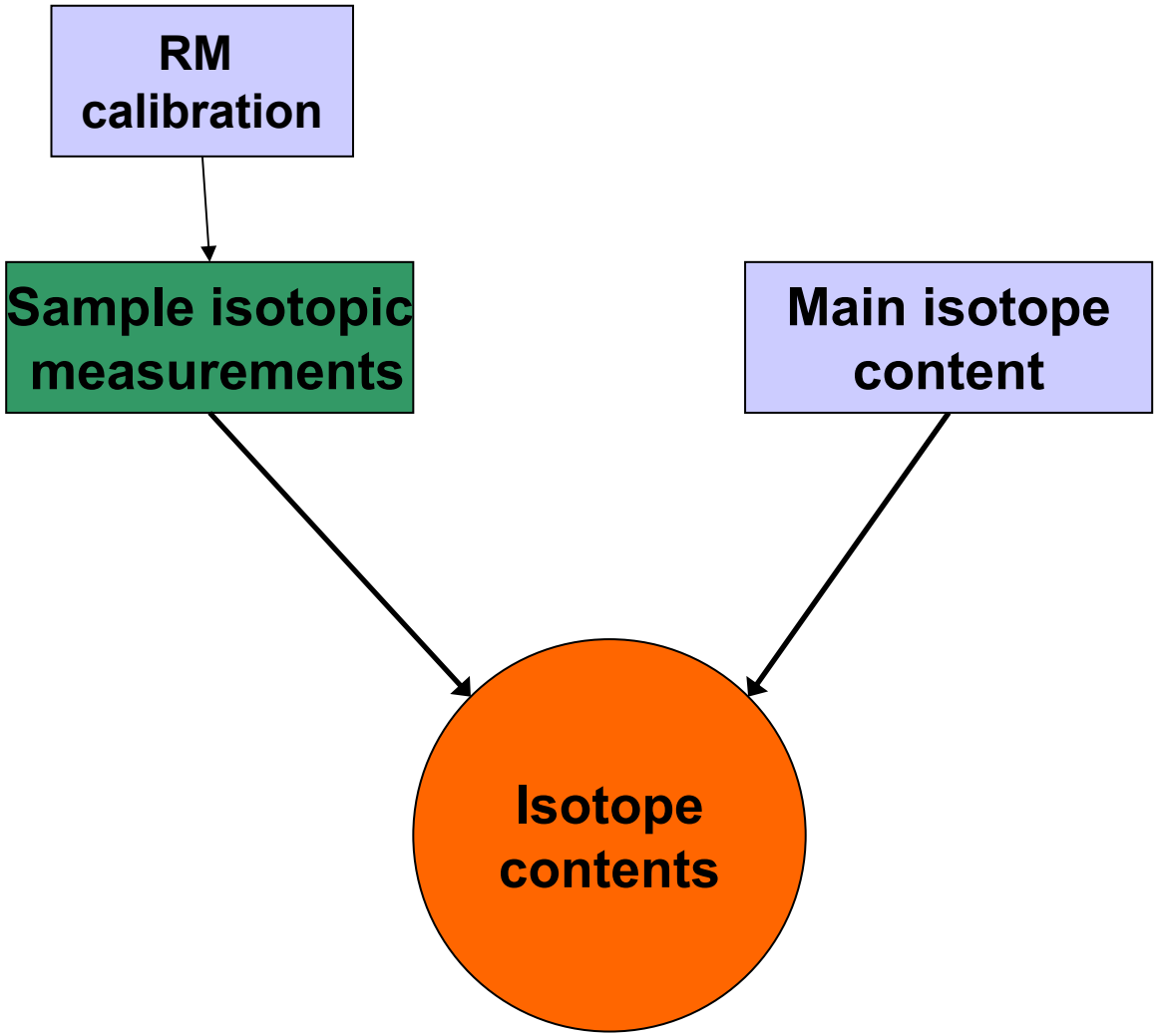
Isotope Dilution Mass-spectrometry



- LSD certificate: amounts
- LSD certificate: ratios
- Sample measurement
- Isotopics
- RM cal

Uncertainty contributions

Isotope Dilution Mass-spectrometry



Amount main isotope (from IDMS)
Isotope calibration
Sample measurement

Isotope dilution with LSD spike

Each measurement is built on a foundation of a reference material = the LSD spike

Do we need repeated measurements?

Not needed

- **One well-controlled measurement is sufficient in principle**
- **Extra measurements bring little improvement to the uncertainty**
- **Measurements must be under QM and <u>transparent</u>**

Needed

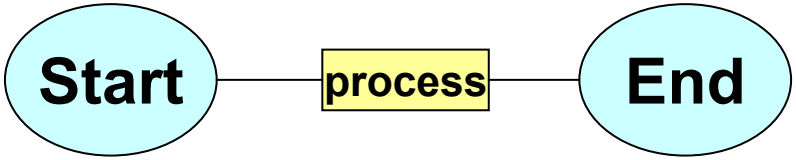
- **Extra measurements increase the trust**
  - Mistakes / blunders
  - Deceit (!)

Do we need LSD spikes with very low uncertainties?

Yes - when values of the isotope contents with the lowest measured uncertainties are required

Yes – when the results are being compared with measured or calculated results done elsewhere on the same sample

No – when a difference between internal samples or input/output of a process are is made



Use of one spike for comparison measurements

Taking a spiked sample and measuring sub-samples always gives results that agree well.

Why?

- Sample problems are eliminated
- A large part of the measured uncertainty coming from the spike is present in each measurement. Large degree of correlation, therefore lower apparent scatter

Practical problems: future development

The development of LSD spikes is still on-going

- **Deposition methods and stability**
- **Different ratios U/Pu (MOX fuel)**
- **Alternative starting materials linked to more flexible application setups**

Deposition methods

- **Present method is not fool-proof (< 100% yield)**
  - Different types of vials?
  - At least partially metals used? – 20% U metal
  - Different covering / higher temperature treatment / addition of other inert materials?
  - Use of robot deposition can increase throughput and increase reliability

U/Pu ratio

- **The present U/Pu ratio (25:1) is a compromise**
  - A lower ratio is maybe required for MOX fuels
  - Ratio is always defined by the ability to measure by mass-spectrometry
  - Separate spikes for U and Pu possible, but:
    - An excess of uranium seems to stabilize the Pu deposit: more work needs to be done on this

Alternative sources of materials

- **Use of primary metals for U and Pu is justified for essential applications of the spikes**
  - Limited supply in medium/long-term
- **Spikes made from U/Pu mixtures (e.g. starting as oxides) need to be certified against reference materials**
  - Consequence is slightly higher uncertainties
  - Easier to obtain materials