

# Some considerations on the role of LSD spikes in safeguarding nuclear reprocessing plants

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## **Abstract**

Large sized dried spikes (LSD) are a fundamental part of the fissile material control of irradiated nuclear fuel. They are applied to measure the uranium and plutonium content of dissolved fuel solutions from reprocessing plants using isotope dilution mass-spectrometry (IDMS). Since the first batch of LSDs was produced, the concept of directly spiking samples of the solution with dissolved irradiated nuclear fuel for later dilution and measurement of the isotopic contents of uranium and plutonium has been developed successfully.

In the method employed at IRMM, very high quality isotopically enriched metals of uranium (natural and high-enriched) and plutonium are dissolved into a single large solution in nitric acid. Individual spikes are then made by aliquoting weighed amounts of the solution into penicillin vials and drying carefully. A light cellulose layer is dried on the spike material to retain the spike at the bottom of the vial during transport to where it will be used. The spikes are prepared in large batches (1000 units) under rigorous conditions [1].

Each spike then has a certified mass of uranium ( $^{235}\text{U}$  and  $^{238}\text{U}$ ) and  $^{239}\text{Pu}$  with an associated uncertainty derived by a rigorous procedure (following the GUM) from the measured and certified parameters of all starting materials and solutions. The plutonium component is highly enriched in  $^{239}\text{Pu}$  and is used to measure the Pu content in the fuel. The uranium component is a mixture of two uranium source materials, natural uranium and a highly enriched uranium component. These materials are mixed to arrive at a final enrichment of just under 20% in  $^{235}\text{U}$ , significantly simplifying transport and handling of the spikes. A series of verification measurements are carried out during the process and the final spikes are certified from the masses of the metal starting materials, the certified assay (purity) values of uranium and plutonium in the starting materials, the mass of the solution, the mass aliquoted into each vial and the isotopic abundances of each of the starting materials.

These spikes are prepared to fulfil the existing requirement for reliable and traceable spikes in fissile material control of dissolved nuclear fuel. The amount content of the spikes is such that no dilution of a typical sample of dissolved fuel is needed before measurement by Isotope Dilution Mass Spectrometry (IDMS) using a single LSD spike. Because each spike is certified for amounts of plutonium and uranium in the vial, the only quantitative step needed at the reprocessing plant laboratory is to weigh as accurately as possible an aliquot of the dissolved fuel solution onto the spike and ensure complete mixing of spike and sample.

The present paper will look at the present method of producing the spikes and look at the optimal method of employing these, both from the point of view of the plant operator and of the safeguard authority. The need for both local production of the spikes and supply from an acknowledged metrology institute will be examined.

The implications of the application of these types of spikes will be looked at; in particular how the results from IDMS carried out with the spikes can be augmented with other measurements, normally using NDA techniques.

Finally the relation between 'independence' and 'traceability', which is a subtle one, often confused, will be considered in specific relation to the application of LSD spikes in the nuclear industry.

### ***Historical development***

The suggestion to use LSD spikes was made over 20 years ago. The intention was to remove a major source of uncertainty in the measurement of uranium and plutonium isotopic content in dissolved fuel solution by providing a spike for subsequent IDMS measurements in which the concentration of the U and Pu were high enough to obviate the need for a preliminary dilution of the hot dissolved fuel solution. The dilution step had long been recognized as one that was difficult to carry out accurately under normal working conditions in hot cells at nuclear fuel reprocessing plants. Moreover, with the increased burn-up typical of modern nuclear reactors, the gamma radiation intensity from fission products in the solution would require a dilution with a large factor to be carried out in 2 steps if the samples were to be handled using conventional glove-box facilities. IRMM first investigated the development of large sized spikes in metal form. Uranium metals, one highly enriched and the other of natural uranium, were blended to produce a 20% enriched material. This was recognized as the optimal enrichment for uranium that could be delivered and handled at the reprocessing plants. Plutonium, enriched to around 95% in  $^{239}\text{Pu}$ , was alloyed with gadolinium to make a 6% alloy by weight. This allowed metal pieces containing around 2 mg  $^{239}\text{Pu}$  to be punched out.

The metal large spikes had some advantages. The metals were simple to check when placed in sealed vials and dissolution of metals when the warm fuel solution was added occurred readily. However the problems of controlling the homogeneity of the plutonium metal alloy were not straightforward, and because the Pu content then had to be subsequently measured (losses of Pu or Gd during the alloying process could not be avoided) and also because producing the spikes in large quantities was technically

difficult this type of large spike was replaced after a few years by the large size dried (LSD) spike.

### ***Production methods at IRMM***

From the point of view of the measurement process, the LSD spikes are classic spikes for IDMS. The amounts of the isotopic enriched materials are designed so that an aliquot of the fuel solution can be added directly to the vial or ampoule containing the spike and a sufficient change in the isotopic ratios for both uranium and plutonium for isotope dilution is guaranteed. After dissolution of the spike and thorough mixing, a small fraction of the solution is taken for subsequent chemical separations and measurement of the isotopic ratios. The chemistry steps are carried out conveniently in glove-boxes. A short overview of the method used for the production of these LSD spikes at IRMM is as follows:

Plutonium metal standard, highly enriched in  $^{239}\text{Pu}$  is weighed and dissolved in concentrated nitric acid and a few drops of conc. HF at sub-boiling temperatures and over a time period of several weeks or months. Natural uranium and high-enriched  $^{235}\text{U}$  metals are individually weighed and added to the dissolved Pu solution. The dissolution of the uranium metals is relatively rapid. The solution is allowed to homogenise and made up to approximately 3 kg in 5 M  $\text{HNO}_3$ . Aliquots of this solution are weighed into penicillin vials and dried at a low temperature. A small amount of an organic material dissolved in acetone is added and dried down. Cellulose acetate butyrate (CAB) is the material presently applied. The organic layer formed prevents the dried spike flaking off during storage and transport but dissolves readily in hot nitric acid and does not leave a residue. The size of the batch of LSD spikes currently produced at IRMM is limited to approximately 3 kg of solution because of handling limitations in the glove-boxes and because this is maximum weight that can be accurately measured with the balances available at present. Between 1000 and 1200 individual spikes are the result of this amount of solution.

Each spike is characterised by the isotopic concentrations of the uranium and plutonium in the 3 kg solution and by the weight of the solution dispensed into the vial.

### **Verification measurements**

After dissolution of the metals is complete and the solution has been made up to the correct weight with nitric acid, at least 6 aliquots are taken and spiked with a certified spike (IRMM-046b) containing  $^{233}\text{U}$  and  $^{242}\text{Pu}$  and the uranium and plutonium content of the solution is then measured by isotope dilution. The isotopic abundances of both elements are measured in an unspiked sample. This is especially important for uranium because it is a check and confirmation of the mixing of the two starting uranium metals. To confirm and verify that there were no changes in isotope amount concentration before and during dispensing into the vials, a random series of vials are taken after drying, spiked with IRMM-046b and the Pu and U contents measured by IDMS.

These verification measurements are part of the quality management of the preparation of the LSD spikes; but the certified isotope contents are derived from the mass metrological values from the starting metals.

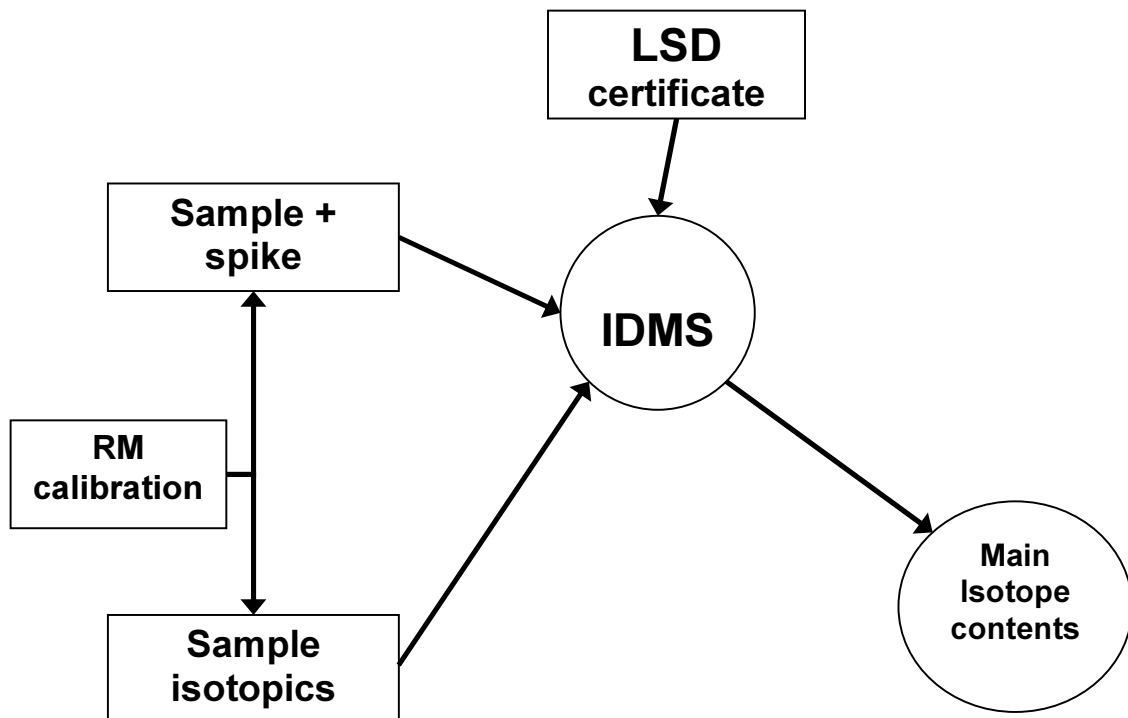
### ***Implications of use of this type of LSD spike***

By producing spikes directly from certified metals, the uncertainty of the isotopic contents of each vial arises only from the certified values of the original metals and the weight of the solution dispensed. This yields an uncertainty traceable in a minimum of steps to the SI. This means that a single spiking with the LSD spike followed by separation of the elements and measurement of the isotope ratios will yield values for the isotope concentrations with a low uncertainty.

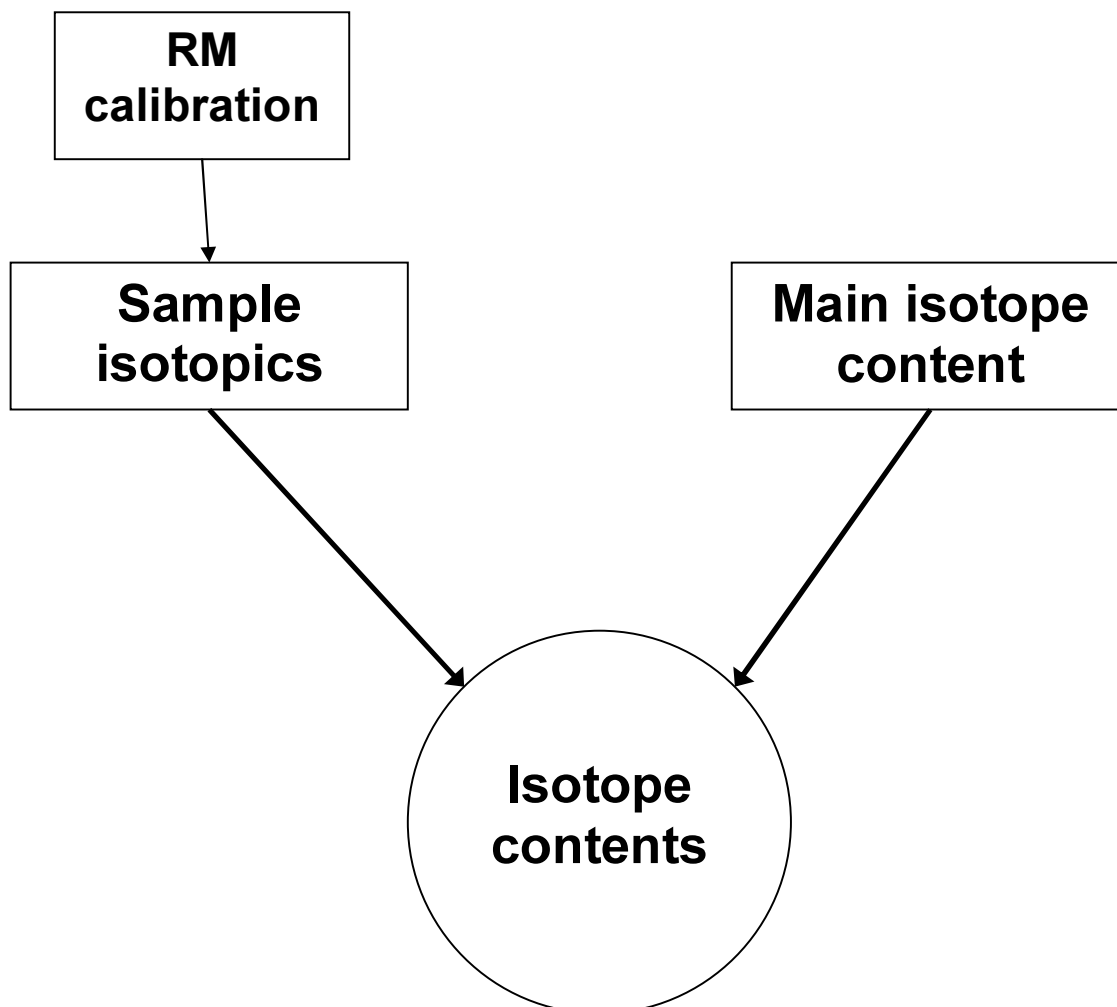
The sources of the contributions to the final uncertainty of the isotopic content of the sample measured by IDMS and applying the LSD spike are shown in Figure 1. The main sources are

- 1 the certified uncertainty of the spike isotope content and the isotope ratio of the LSD spike
- 2 the measured isotopic ratio in the spiked sample
- 3 the measured isotope ratio in the sample (unspiked)
- 4 the weight of the sample

For the measurements performed on the sample, spiked and unspiked, there will also be a contribution from the mass-calibration of the mass-spectrometer, which will depend on the method employed in the measurement and also on the certified values of the isotopic reference material used for the calibration.



**Figure 1: Sources of uncertainty in measurement of the content of the main isotope by IDMS using the LSD spike**



**Figure 2: Sources of uncertainty for the measurement of the sample isotope contents**

After measuring the main isotopes of uranium and plutonium in the sample (i.e.  $^{238}\text{U}$  and  $^{240}\text{Pu}$ ) by IDMS the other isotopes of the two elements are measured relative to these. There is therefore another source of uncertainty, coming from this measurement and the associated calibration of the instrument (Figure 2).

Because the LSD spike contributes considerably to the overall uncertainty, depending on the mass-spectrometric skills applied for the isotopic measurements in the spiked and unspiked samples, the best results, in the sense of having the lowest uncertainty of the final isotope contents, will be found applying an LSD spike with a short traceability chain, such as produced at IRMM.

### **Should repeated measurements be made using these spikes?**

As stated above, a single, well-controlled, IDMS measurement using the LSD spikes described here will yield a result with an uncertainty that is as low as can be achieved by this technique. Repeated measurements on sub-samples spiked independently with further LSD spikes will in general not significantly reduce the uncertainty on the measured

isotopic content because one of the main contributors of uncertainty, the spike itself, is common each time.

Multiple spiking of samples is commonly done to check the homogeneity of the samples – in other words to assure the analyst that the results made on the sample are typical of the main solution and therefore can be applied to the declarations of the total dissolved fuel. It can also be done as a safeguards measure to ensure that correct sampling, weighing and spiking were carried out. It is our contention that the LSD spikes described here, using very high quality metals, which for Pu especially are in short and limited supply, should not be used to check for sampling errors or lack of homogeneity in the main solution. Other methods can be applied for this - which remains a task to define and organise in the future.

The safeguards considerations mentioned above can legitimately demand multiple sub-samples and independent spiking but it should be recognised this comes with a high price. It is our opinion that a more flexible scheme using LSD spikes from different sources could be used to ensure that safeguards criteria are met. Again such schemes still need to be proposed and applied: a task for the future.

### ***Developments for the future***

The application of LSD spikes has been highly successful, as seen by the growing demand for future supplies. However, both the practical, i.e. preparation side and the application methodology can be improved in the future.

### **Practical developments**

The present methods to prepare LSD spikes are relatively successful but can still be considered as under development. Feedback from the users of the spikes have shown over the recent years that changes to the ampoules, to the chemical form and to the form of the certificates could improve the handling of the spikes at the reprocessing facilities.

The long-term stability of the spikes is still a cause for concern. Flaking of the dried material still occurs and may be dependent on the storage environment and possibly the effect of radiation over time. Control measurements carried out at IRMM, to be published in 2008, have shown however that even the oldest of the archived spike samples still retain the certified values (within the measurement uncertainty of IDMS) .

Changes in organic covering may improve the long-term stability, although this could have a possible effect on the chemistry of the spike-plus-sample and therefore should only be introduced after thorough examination and testing. Other forms of deposition are also under consideration and a robotised aliquoting and weighing system has been tested and validated at IRMM recently.

The batches are individually certified, which raises the possibility that small differences between one batch and the next – within the certified uncertainties – could be present and visible under certain forms of application at installations that use large numbers of the spikes. A continuity check between one batch and the next is under consideration at IRMM.

### **Changes to the methodology of application**

The present methodology is to use the ‘best’ spikes as often as possible and sometimes in multiple applications of sub-samples, as discussed above. The effort needed to produce

the spikes and the reliance on the very high quality certified metals as base materials is an argument to apply the spikes exactly where needed and to back them up with other methodologies. Some possibilities are:

- The use of locally produced spikes could play a big role in reducing the need for the present LSD spikes. Inevitably these spikes would not use the primary metals (adequate supplies of high enriched oxide exist for Pu for instance) but would be certified against other certified materials. Such spikes would be ideally applied to measure homogeneity in samples; in independent measurement of samples where the intention is not to be in competition with measurements done using very high quality spikes but in a verification function; or to measure difference in process control or in method development.
- Rationalisation of the use of the LSD spikes and concentrating on a single well-controlled spiking step, after which possibly sub-samples and independent measurements could be done.
- Re-evaluating the independent measurements carried out by the facility's analytical department on the one hand and the safeguards organisation(s) on the other. These measurements should be looked at in the light of the uncertainty sources to evaluate to what extent the measurements are independent.

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[1] A. Verbruggen, A. Alonso, R. Eykens, F. Kehoe, H. Kühn, S. Richter, R. Wellum, Preparation and certification of IRMM-1027i Large-Sized Dried (LSD) Spike, Report EUR 22611 EN, European Communities, 2006