



## ISOTOPE DILUTION ANALYSIS

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The aspects of isotope dilution analysis that I wish to cover in this lecture are as follows.

- 1) Fundamental aspects of the technique.
- 2) Elements of interest in the nuclear field.
- 3) Choice and standardisation of spike nuclide.
- 4) Pre-treatment to achieve
  - (a) isotopic exchange
  - (b) chemical separation
- 5) Sensitivity.
- 6) Selectivity.
- 7) Accuracy.

### 1. FUNDAMENTAL ASPECTS OF THE TECHNIQUE.

The term isotope dilution analysis refers to any method which involves the addition of a known quantity of an isotope of an element of a different relative isotopic composition to that found in a sample. Measurement of the isotopic ratio of that element before and after spiking with the material of different isotopic composition enables the mass of that element in the sample to be calculated. Although in the strictest sense, the spike isotope could be radioactive as well as stable, my remarks will be confined to the use of stable or near stable materials. For this conference my remarks will be confined to what is known as stable isotope dilution analysis where the isotopic ratios are measured using a surface ionisation mass spectrometer. Some of the elements measured and some of the spike nuclides used are, however, in the strictest sense radioactive materials.

Five basic steps are involved in isotope dilution analysis.

#### Operational steps in isotope dilution analysis

- 1) Sample dissolution.
- 2) Sample dilution and spiking

- 3) Isotopic and chemical exchange.
- 4) Chemical separation.
- 5) Isotopic composition measurement by mass spectrometry.

## 2. ELEMENTS OF INTEREST FOR ISOTOPE DILUTION ANALYSIS IN NUCLEAR CHEMISTRY.

- 1) Uranium - burn-up, safeguards, reprocessing
- 2) Plutonium - burn-up, safeguards, reprocessing, nuclear decay data
- 3) Neodymium - burn-up
- 4) Other rare earths - burnable poisons, control rod materials, fission yield measurement
- 5) Boron - burnable poisons
- 6) Caesium - fission product behaviour in fuel, standardisation
- 7) Thorium - burn-up
- 8) Other elements - Mo, Zr, etc. fission yield measurements.

These elements are restricted to those of importance in the nuclear power programme and excludes geological applications. It also excludes gaseous elements and volatile elements such as lithium and cadmium, either because they are not measured by surface ionisation mass spectrometry or because they are very rarely measured by isotope dilution analysis.

### 3. A. Choice of spike and monitor nuclides.

Most of the elements of interest to be measured by isotope dilution analysis are poly-isotopic. In the ideal case then a spike nuclide is chosen which is not present or present only to a very small amount in the element of the sample to be measured. For example, in the case of the measurement of uranium, the isotope of mass 233; will be added as the spike nuclide because it is not present in natural uranium or in uranium associated with most reactor uses. It would be measured against either isotope with mass 235 or 238. If thorium had been present in the nuclear material before irradiation then a correction would have to be made for the amount of 233-uranium present by measurement of the isotope composition without the addition of the spike. Use of spike material which is not mono-isotopic but which is of different isotopic composition for the same element in the sample to be analysed leads to a sacrifice of overall accuracy of the method. Again in the ideal case

a spike nuclide will be added in an amount such that it leads to as near as possible a ratio of one for the spike and the monitor nuclide. In some cases this could result in the spike and the monitor nuclides being less than other isotopes in the mixture. For example, in the case of neodymium, the isotope of mass 148 is frequently the preferred monitor nuclide for burn-up measurements. The fission yield of the 148 isotope is lower than 143, 144, 145 and 146 nuclides, and if the 142 isotope is used as spike attempts will be made to add sufficient 142 to equal the 148 mass for the measurement. However, in most cases a guess must first be made of the concentration of the monitor nuclide since the object of the exercise is to measure its mass. Providing this guess is correct within a factor of ten for the amount of spike isotope there will not be a significant increase in the error of the measurement with modern mass spectrometers.

The following spiking nuclides are being used for isotope dilution measurements of elements of greatest importance to the nuclear fuel analysis field.

(a) Uranium

The isotope of mass 233 is the nuclide of greatest importance since it is not normally present in natural uranium or irradiated uranium fuel. It is two and five mass units away from the isotopes 235 and 238 which are the major monitor nuclides so that some knowledge of the mass discrimination effects of the mass spectrometers must be known. Isotope of mass 236 has had a very limited use as a spike isotope and its greatest usefulness is its use with isotope 233 as double spike. The mass discrimination can be virtually eliminated using this technique since it has the same difference as 235 and 238.

(b) Plutonium

The isotope of mass 242 has been the favoured isotope to date because of its availability in highly enriched form. However, its fractional presence in plutonium increases with the irradiation of the plutonium so that in highly irradiated fuel for the highest accuracy or to avoid the necessity of measuring the plutonium without added spike nuclide to obtain the isotope composition, the next stable isotope of mass 244 is now being used. This too is becoming available in increasing quantities in a highly enriched form. There is some difficulty experienced in obtaining highly enriched 242 and 244, the isotope 238 obtained from the decay of separated curium can be used.

(c) Neodymium

For burn-up measurements two spike nuclides have been used. One is enriched isotope of mass 150 and the other of mass 142. Use of mass 150 enables a check to be made of natural contamination and is only 2 mass units away from the thermal fission monitor nuclide of mass 148.

However, its use necessitates the measurement of spiked and unspiked neodymium in the sample. Isotope of mass 142 is however produced in fission to a limited and variable extent from neutron capture of praseodymium-141 so that all of the 142 mass found cannot be attributed to natural contamination. In fast reactor irradiations of mixed uranium and plutonium fuel neodymium-143 is the preferred burn-up monitor and neodymium of mass 142 would then be a preferred nuclide for spiking.

Many of the spikes used for isotope dilution analysis are mixed together where more than one element is measured regularly. For example,  $^{233}\text{U}$ ,  $^{242}\text{Pu}$  and  $^{140}\text{Nd}$  (or  $^{142}\text{Nd}$ ) are often used as a mixed spike for burn-up measurements. This technique should reduce errors from aliquoting and improve the overall accuracy of the measurement providing the ratios are reasonably close to those of the monitor nuclides in the samples to be measured. For routine measurements of samples of similar burn-up of the same fuel type and reactor irradiation this technique has distinct advantages. Where a wide variety of burn-up values and fuel types are encountered its use is of limited applicability.

3.B. Calibration of spike nuclide.

One of the two largest sources of error in the isotope dilution analysis technique comes from the calibration of the spike nuclide. In the ideal case the spike nuclide should be calibrated against a standard of the element to be measured of the same isotopic composition of the element to be measured in the sample using the isotope dilution technique. This is by no means always possible, or always desirable for some standard materials, for example, mass standards of plutonium should have as low a  $^{241}\text{Pu}$  content as possible because of its short and not very well known half life. Standards can be made up for calibration from highly purified elements or compounds of known chemical composition and sub-

sequently standardised by an alternative independent technique. For the highest accuracy this latter step is essential, for example, coulometrically. In all cases weighed aliquots of spike and standard solutions should be mixed, rather than volume fractions.

The standard materials used are as follows:

- A. Uranium - metal,  $U_3O_8$   $UO_2$  - or prepare solution and standardise
- B. Plutonium - metal,  $PuO_2$   $U(SO_4)_2$   $Cs_2UCl_6$  - or standardise
- C. Neodymium - metal,  $Nd_2O_3$  - or standardise.

#### 4. CHEMICAL PRE-TREATMENT

The first step in the analysis of an element by isotope dilution, is to obtain a representative sample. In the majority of applications for the elements of interest, sensitivity is not a problem because of the inherent high sensitivity of the surface ionisation technique and the need to take samples which are truly representative of the parameter to be measured. One notable exception is that of the measurement of the fissile material obtained from the fall-out from a detonated nuclear weapon.

Most of the samples from a nuclear reactor fuels programme require to be handled initially using shielding and remote handling techniques. This necessitates the use of lead or concrete shielding cells and remote handling manipulators to dissolve the sample and take representative fractions.

Cleaning glassware and other equipment in shielded cells is a very difficult operation, consequently in order to minimise the risk of cross contamination clean glassware is used for each dissolution, dilution and separation step. As far as possible, this standard laboratory glassware which has been cleaned by soaking in 8N nitric acid for several days, followed by demineralised water and oven drying. As far as possible simple dissolution procedures are carried out but care must be taken to ensure complete solution of all of the fissile and fission product material. In order to simplify subsequent separation methods, cladding material is only etched with the reagent and not completely dissolved. Some material such as the high temperature coated particle fuel has to be crushed to ensure that the reagents can dissolve all of the nuclides of interest in the sample. For samples which have proved to be very

resistant to normal dissolution procedures specialised methods such as sealed quartz tube or pressure dissolution have been employed.

The amount of an element required for measurement of isotopic composition is never more than a few micrograms using all types of present day mass spectrometers. Since the amount of sample taken is of the order of several grams to ensure that local variations in homogeneity of the nuclides of interest are representative, considerable dilution of the sample has to be made prior to spiking and chemical separation. This again is best done by weighing the solution and subsequent small fractions or aliquots before diluting with a similar strength acid medium. This diluting may have to be carried out several times before the appropriate amount is readily removed from the shielded facility. Aliquots of spike and sample can then be made by again weighing portions to achieve the highest accuracy. In the case of mixed spikes where the ratio of nuclides only is required, this latter step is not necessary.

The second major source of error that exists in the operation of the isotope dilution method of analysis is the achievement of isotopic exchange, or lack of it, between the spike nuclide and the nuclide to be measured. The mixing of two solutions, one containing the spike and the other the sample, does not automatically bring about isotopic exchange. Consequently, even the simplest of chemical operations to prepare the sample for isotopic analysis in a mass spectrometer can lead to a change in the ratio of the two species. It is therefore necessary to ensure that all of the isotopes of an element are in the same valency state and the same state of complexing as soon as possible after mixing spike and sample. It cannot be assumed that solutions of sample or spike are stable for indefinite periods particularly if significant amounts of radioactive materials is also present. For elements such as plutonium, which has the property of existing simultaneously in three different valency state in solution, vigorous oxidation and reduction steps must be carried out on the mixture to ensure isotopic exchange. It must also be remembered that actinide elements are readily hydrolysed so that complete solution must also be ensured before this redox exchange is attempted. The presence of complexing anions such as fluoride, phosphate, chloride, sulphate, and in the case of uranium, carbonate can all prevent exchange occurring unless again the solution is sub-

jected to sufficiently vigorous treatment to break up these complexes. A useful standard procedure then has been found to consist of a double evaporation to dryness with nitric acid followed in the case of plutonium by reduction and oxidation steps prior to chemical separation.

Chemical separation is necessary to remove other radioactive species, other nuclides with interfering isobars, other extraneous material which is likely to influence the mass spectrometric analysis. Ideally only the element to be measured should be placed on the filament of the mass spectrometer emission source. Separation procedures have to be found which are:

- (a) specific to the element to be measured
- (b) capable of a high degree of reproducibility, since in many cases there is no indicator present of the element to be separated
- (c) can be carried out on microgram quantities of material very simply
- (d) does not introduce any other interfering materials.

Methods that are used successfully include - ion exchange chromatography reversed phase partition chromatography, solvent extraction, and precipitation. These separation procedures can be operated for the isolation of only one element or sequentially to isolate several elements that are to be measured by isotope dilution analysis. Ion exchange chromatography is undoubtedly the most favoured technique mainly because its adaptability to very small quantities of both reagents and the element to be separated..

## 5. . SENSITIVITY

A very important aspect of the isotope dilution analysis technique is its inherent very high sensitivity for a wide range of elements. This sensitivity will vary for the different elements depending on their volatility and ionisability. The efficiency of the ion optics, the resolving power, and the detection system are features of individual mass spectrometer designs and have been improved very considerably in recent years. Except in a few isolated requirements, sensitivity is not a limiting feature of the technique as applied to nuclear problems. Whilst nanogram quantities of both actinide and rare earth elements are routinely measured most operators employ microgram quantities to

reduce the errors from reagent and material blanks and risks of cross contamination from one sample to another.

## 6. SELECTIVITY

Again another very useful feature of the isotope dilution analysis technique is its selectivity and capability of being operated over a wide range of concentrations. This selectivity is derived from the ability to apply chemical separation procedures not requiring complete recovery of the element of interest, and from the difference in volatility and ionisation.

## 7. ACCURACY

The inherent achievable accuracy for isotope dilution analysis will depend on the errors associated with a number of variables. The biggest sources of error, as previously stated arise from the calibration errors of the spike nuclide, the exchange between sample and spike, pre-chemistry and source preparation, and to a lesser extent machine stability and data. It has been shown by a number of investigators that + 0.17 accuracy is achievable under very carefully controlled conditions. Under routine operation + 0.5% can be obtained and maintained with skilled operators. Unfortunately in practice, interlaboratory comparisons such as the IDA 72 experiment indicate that between laboratories accuracy when inexperienced laboratories are also included is nearer to + 2%.

Discussions after the introduction of A. Fudge

Perrin: I must disagree with the statement that the stoichiometry of  $U_3O_8$  is unprovable. Mr. Marklin at NBS and Mr. Waterbury at Los Alamos had for years this running problem that, using the same ignition procedure at Los Alamos (8000 feet altitude) and NBS (nearly sea level) produced a 0.2% bias. Mr. Marklin developed a procedure whereby the uranium oxide is ignited at a  $1000^\circ C$  in a stream of oxygen. The furnace is turned off and the sample is allowed to cool down in the oxygen atmosphere. The stoichiometry was reproducible better than 0.005%. The exact stoichiometry was demonstrated by dissolving the material and titrate the uranium by weight titration (Davies and Gray). The reproducibility was better than 0.006%.

Fudge: We too at Harwell were interested in uranium oxide especially the U/O ratio. We have examined the metal-oxygen ratio for uranium quite extensively. It was clearly showed that there was not such a compound as  $U_3O_8$ . We have tried various receipts including the one you have mentioned. It was shown that with very little changes in the procedure you can get substantial changes in the stoichiometry. I agree that when you are very careful you can get a product that is good enough. But I warn people who just take something out of the bottle and heat it without precaution. Without any care your error will be as large as 0.25% with some care it may be better than 0.1%.

Bases: I certainly agree that  $U_3O_8$  is not a compound. The only thing we do is producing a reproducible product. You seem to suggest  $UO_2$  as an alternative. I think  $UO_2$  is a difficult thing to keep around.

Judge: We have had no difficulty in maintaining  $UO_2$ : Certainly we have showed that it is able to keep its form better than  $U_3O_8$ . A disadvantage is its poorer solubility in nitric acid.

De Bieure: We have investigated a number of  $UO_2$  samples and found differences in the stoichiometry between manufacturers measurements and ours.

Scarborough: The metal U is the best base for the reference material for it can be cleaned up as received. The standards of NBS has to be cleaned up before use and this is a simple operation. In the case of

$U_3O_8$  I agree with both points of view, I am somewhat in the middle. If the same source of  $U_3O_8$  is used, the same procedure exactly repeated, you can reproduce the same stoichiometry. If the sources are different this poses a problem, you will obtain offsets from other materials. The whole procedure, all steps, effect the stoichiometry of the material. However the  $UO_2$  needs protection from the environment throughout its use. When you accomplish your atmospheric protection you are in a good shape. There is the problem with the moisture which is difficult to handle. Especially the atmospheric differences from plant to plant f.i. the controlled ones against the uncontrolled ones.

*Barnes:* We have recently faced the problem of using  $UO_2$  as a standard. The only acceptable system is the high fired one which is so difficult to dissolve that people feel perhaps that they have more problems of getting that in solution then getting a  $U_3O_8$  with reproducible stoichiometry.

*de Bieure:* You said in your introduction that you needed a maximum contrast in isotopic composition between spike and sample, is that necessary?

Secondly at one point you stated that you double the error when you measure the 150-Nd in the unknown sample and in the spiked sample which makes up for two times the error. In all isotope dilutions the error in the spike ratio measurement, that is the measurement of the ratio of the nuclide of the unknown sample to the nuclide of the spike is the only real error contribution.

Thirdly you want to calibrate against a sample of the same isotopic composition, I do not think that is completely true.

*Fudge:* What I stated was the ideal situation. When you want to make an isotope dilution analysis you want the difference between sample and spike to be as large as possible. In this world you can not have always an ideal situation, you have to compromise. On the other hand in this real world we have to deliver a certain amount of work. In our situation we can not afford spending a long time on one sample. This implicates that concerning the spike you will choose the most optimal case to decrease the component in the error due to the spike composition.

Also about standardization I was talking from the ideal situation. In practice often you do not know the isotopic composition of your samples.

Concerning the 150-Nd-spike there must be a double error. You have to measure spike and sample.

*de Bièvre:* When your mass spectrometer is in good shape the error is constant over a range of ratio values (f.i. from 0.1-10). This means that within this range conditions are optimal and it is not necessary to spike 1 : 1.

*Barnes:* You bring in a different point about what ratio you need to spike. Actually what was said was that in the ideal case you want your spike to be as different as possible. Take the case of vanadium with one isotope 99.75% and the other 0.25%. The ideal spike would be one to be the reverse of that. I do not need to spike 1 : 1 exactly to get a good measurement but that is another thing. The reversed composition will be my ideal spike, for the measurement of the spike composition becomes a trivial part of the whole operation. I do not have to worry about the isotopic composition when one isotope is 99.75% and that is the ideal case. I agree that it is not strictly necessary but if I had the choice I should make it and that was what I meant.

*de Bièvre:* One can spike a low enriched uranium sample with 93% or 80% enriched 235-uranium. This does not add to the uncertainty and is not worse than spiking with 233-U. Imagine that one measures an unknown 2% low enriched uranium and one spikes it with 235-U. One would calibrate optimally the spike with a well-known standard of 2% enriched. In my opinion that is not required and one can better calibrate with a 1% or even a natural uranium.

*fudge:* I think a lot of this is academic. Let us go back to the real world. This is the situation (showing a slide of IDA-72) with differences up to 20%. This is the real situation and do not talk about 0.1% difference.

*de Bièvre:* I agree with that completely and I hope the isotopic people will improve that with the IDA-78 experiment.