

TECHNICAL SHEET ABOUT (NUCLEAR) MASS SPECTROMETRY

1. Objective of the Technique:

Mass spectrometry is the most commonly used Destructive Analysis (DA) technique in nuclear safeguards for measuring the isotopic composition and isotopic amount content (concentration) of uranium, plutonium and other actinides in a sample.

2. Presentation of the Technique

2.1. Principle of measurement / Definition of the physical principle

For an analysis using a mass spectrometer a given sample is first

- introduced into the ion source (by various techniques, e.g. gas flow, nebuliser, sample magazine) and
- ionized (by various techniques, e.g. hot metal filament, plasma, ion beam),

The ions of the sample are then

- accelerated (usually by high voltage),
- separated by mass (by various techniques, e.g. using magnetic and or electric field, or time-of flight system), and
- detected (by various techniques, e.g. Faraday cups or Secondary Electron Multiplier).

Depending on the type of instrument and on the application, the detected ion current intensities obtained from an analysed sample can be used to calculate the *elemental* or *isotopic ratios* of the sample from which the *elemental* or relative *isotope abundances (isotopic composition)* are derived.

As an example, in Fig.1 the mass spectrum of a natural uranium sample is shown. By ramping the magnetic field strength, the mass range from $m=233-239$ a.m.u (atomic mass unit) is scanned through a Faraday cup detector. The isotopic abundances are proportional to the measured ion currents displayed on the graph. The ion currents as measured for a sample of natural uranium are displayed in logarithmic scale, in order to cover the large dynamic range of the uranium isotopic abundances.

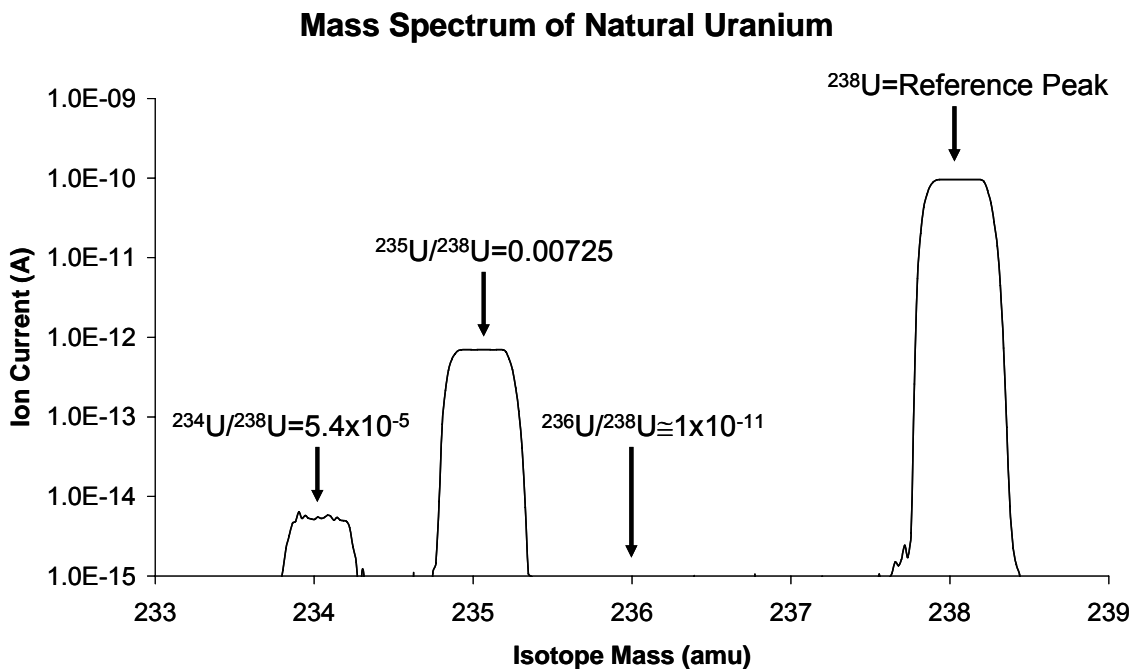


Fig.1: Mass Spectrum of Natural Uranium

Many nuclear material samples contain different elements with isotopes of similar mass, for example ^{238}U and ^{238}Pu . In such cases, either the mass spectrometer must have sufficient mass resolution to be able to distinguish between these isotopes, or the sample must be treated chemically (e.g. by ion exchange chromatography) to separate the different elements prior to the mass spectrometric measurement.

A second complication in the application of mass spectrometry is the potential presence of mass fractionation effects. These arise because different isotopes of the same element do not undergo the processes such as evaporation, ionisation and detection at the same rate, for given ion source conditions. Depending upon the mass spectrometer used and the procedures applied, mass fractionation effects may need to be corrected for through the measurement of certified standards and application of a correction factor derived from these standards to all results obtained.

The element amount (concentration) within the sample may be calculated through a process known as isotope dilution mass spectrometry (IDMS, see below). This involves the addition of a known amount of one particular isotope ("spike") of the element of interest. By mass spectrometric determination of the isotopic composition of a sample before and after the addition, the change in isotopic composition can be used to calculate the concentration of the element within the original sample.

2.2. Types of Mass Spectrometers

In order to cover various analytical needs about half a dozen of variants of mass spectrometry have been developed using different combinations of ionisation method, mass separation and detection. This has crystallized in a variety of instrument types which are useful particularly for modern nuclear safeguards:

- AMS accelerator mass spectrometry [1]
is applied in particular, when large isotope abundance ratios are to be measured, for example $^{236}\text{U}/^{238}\text{U}$ in natural uranium (Figure 1).
- ICPMS: inductively coupled plasma mass spectrometry [2], is applied for measuring elements with high ionisation potential and as multi-element analysis method, both for quantitative elemental analysis and isotope ratio analysis. The 3 most important subtypes are:
 - ICP-QMS: quadrupole-ICPMS
the most common type of ICP-MS in routine elemental quantification. Applied for isotope ratio measurements when no high precision (better 0.1 % RSD) is required. Sometimes equipped with a reaction cell to resolve spectral interferences.
 - ICP-SFMS sector field ICP-MS (also referred to as HR-ICPMS (high resolution ICPMS))
for ultra low level elemental quantification and isotope ratio measurements. A magnetic sector field ICPMS enables isotope ratio measurement with a precision better than ICP-QMS. The high resolution capabilities allow the resolution of spectral interferences up to a mass resolution of $m/\Delta m$ of 12.000).
 - MC-ICPMS: multi-collector-ICPMS
allows simultaneous detection of several isotopes, thus enabling high precision measurements. Modern instruments are equipped with higher mass resolution capabilities ($m/\Delta m$ of about 4.000) for interference separation (see ICP-SFMS).
- GSMS: gas source mass spectrometry [3]
is applied for highly accurate isotope ratio measurements of gaseous samples, in particular for uranium hexafluoride UF_6 , an important compound in the enrichment process.
- RIMS resonance ionisation mass spectrometry [4]
allows the selective ionisation of predefined species within a mixture of elements. RIMS makes use of lasers of defined wavelength for the selective ionisation.

- SIMS: secondary ion mass spectrometry [5]
allows isotope ratio measurements of individual particles and has found widespread application in particle analysis for safeguards.
- TIMS: thermal ionization mass spectrometry [6]
is the most widely applied analytical technique for analysing samples of nuclear material.

A more comprehensive publication about isotope mass spectrometry is given in [7].

2.3. Analytical tasks in Nuclear Mass Spectrometry and Associated Types of Mass Spectrometers

- Elemental abundances: these are most frequently determined using TIMS or ICPMS in combination with IDMS (Isotope dilution mass spectrometry [8]: sample is mixed with certified isotopic spike, the change in isotopic composition is used to determine elemental amount content)
- Isotopic amount content (isotopic assay): most commonly determined using TIMS, ICPMS, RIMS, in combination with IDMS (Isotope dilution mass spectrometry)
- Isotope abundance ratios: done using all mass spectrometer types mentioned in section 2.2., but for particular tasks/sample types particular types are being used preferentially, see table below:

Sample Type	Measurand	Instrument Type
U in solution	Isotopic composition	AMS, ICPMS, GSMS, RIMS, TIMS
U in solution	Isotopic comp., in particular $^{235}\text{U}/^{238}\text{U}$ ("major ratio")	ICPMS, TIMS ¹
U in solution	Isotopic comp., in particular $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ("minor ratios")	TIMS, ICPMS, AMS ² (only $^{236}\text{U}/^{238}\text{U}$), RIMS ³
U in UF ₆ gas	Isotopic comp., in particular $^{235}\text{U}/^{238}\text{U}$ ("major ratio")	GSMS ⁴
U or U-oxide particles	Isotopic composition	SIMS (directly), TIMS (if loaded on filament) ICPMS (using LASER ablation)
Pu in solution	Isotopic composition	ICPMS, TIMS
Pu or Pu-oxide particles	Isotopic composition	SIMS (directly), TIMS (if loaded on filament) ICPMS (using LASER ablation)
Other actinides	Isotopic composition	TIMS, ICPMS

¹ in TIMS usually by total evaporation, to minimize mass fractionation effects

² AMS has the lowest possible background for ^{236}U

³ limited capabilities

⁴ in GSMS using double standard method

For almost all instrument types and techniques, certified reference materials are needed for instrument calibration and/or quality control. In particular, they may be required in order to correct for mass fractionation effects. Reference materials certified for isotopic amount content and/or isotopic abundance ratios can be obtained from laboratories specialised in their certification, including the IRMM (<http://www.irmm.jrc.be/html/homepage.htm>) or NBL (<http://www.nbl.doe.gov>).

3. Useful References

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