Accurate and precise ^{235}U quantification by combining isotopic dilution method and ICP/AES measurements

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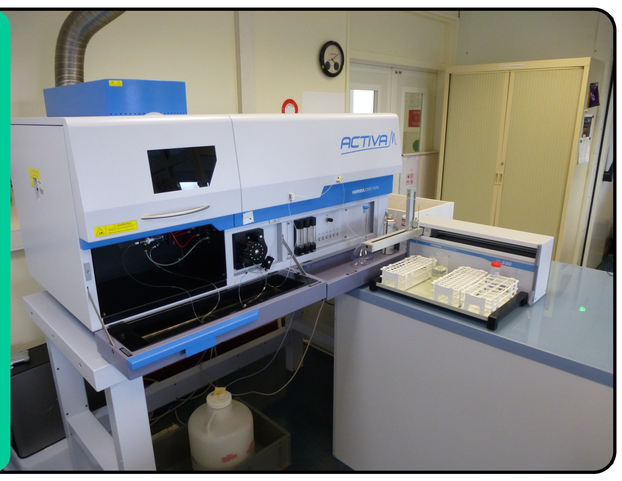
Introduction

Isotopic dilution method is currently applied to ICP/MS measurements (IDMS). Nevertheless, an ICP/AES owning a high resolving power is able to measure the isotopic shift in emission atomic lines for heavy elements such as uranium. Uranium isotopes, such ^{235}U and ^{238}U, are therefore clearly separated and identified. Using this phenomenon, the accurate and precise quantification of uranium or its isotopes is possible. Indeed, the transposition of IDMS method to our ICP/AES instrument allows to quantify, with trueness and precision, the amount content of ^{235}U of an uranyl nitrate solution. The method is named **IDAES** for "Isotopic Dilution Atomic Emission Spectrometry". In this study, the accuracy and precision of the ^{235}U quantification by IDAES are compared to those obtained by IDMS using a MC-ICP/MS instrument.

Instruments

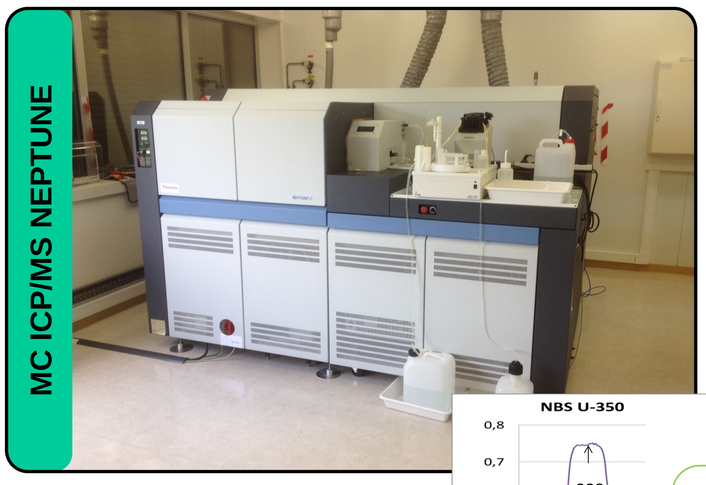
ICP/AES ACTIVA M



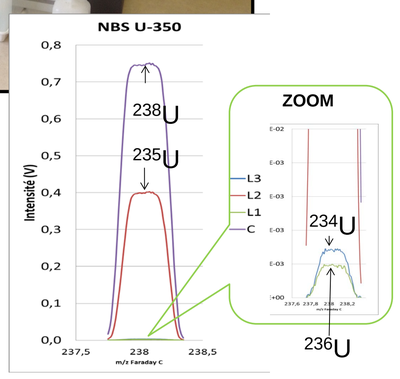
- spectral windows up to 8 nm
- **simultaneous measurement** of multiple lines and backgrounds
- resolution equal to 10 pm in the range of 120-430 nm

	ICP/AES	MC ICP/MS
Plasma parameters		
Radio frequency	40 MHz	27 MHz
Forward power	1000 W	1200 W
Argon gas flow rates		
Plasma gas	12 $L.min^{-1}$	15 $L.min^{-1}$
Nebuliser gas	0.9 $L.min^{-1}$	0.945 $L.min^{-1}$
Auxiliary gas	0.15 $L.min^{-1}$	0.70 $L.min^{-1}$
Acquisition parameters		
Spray chamber	Quartz cyclonic	Quartz tandem spray chamber (combination of a cyclonic and a Scott-type spray chamber)
Nebuliser	Concentric nebuliser	Self-aspirating PFA concentric nebuliser
Sample uptake	1 $mL.min^{-1}$ (peristaltic pump)	150 $\mu L.min^{-1}$ (self aspiration)
Integration time	10 s	8.392 s
Number of replicates	10	30
Collection mode	Not applicable	static

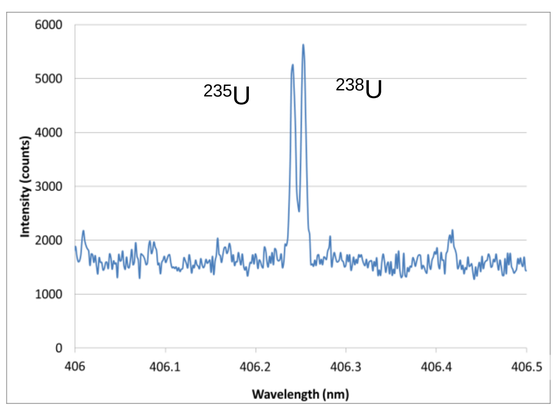
MC ICP/MS NEPTUNE

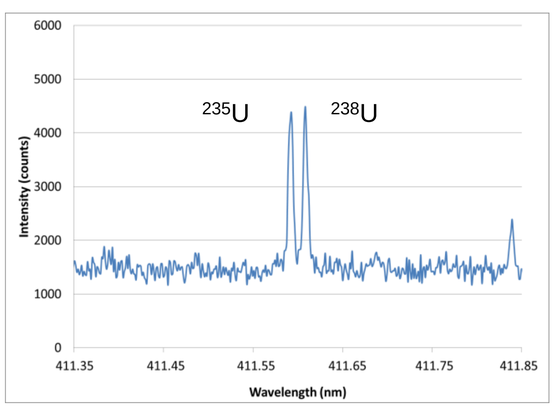


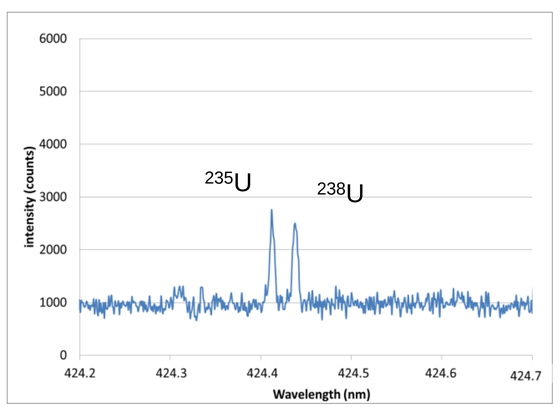
- double focusing Nier geometry
- 9 faraday cups
- **Simultaneous measurements**



Optimum wavelenghts for ICP/AES measurements





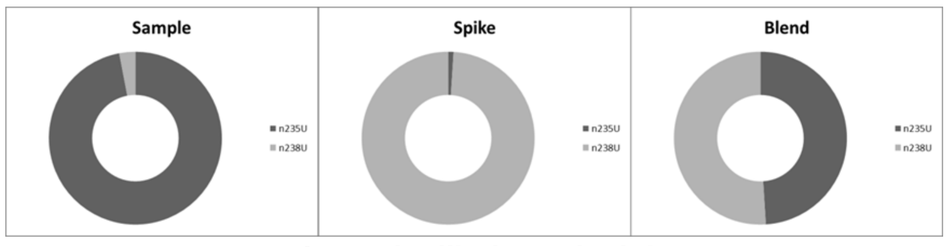


SRM U-500 (5 $mg.L^{-1}$)

Wavelengths used (nm)		Gap between peaks (pm)
^{235}U	^{238}U	
406.241	406.253	12
411.593	411.608	15
424.412	424.437	25

Taking into account a resolution of 10 pm and a fully baseline separation between U splitted lines, 424 nm wavelentgh region is used for ^{235}U and ^{238}U measurements

IDAES and IDMS



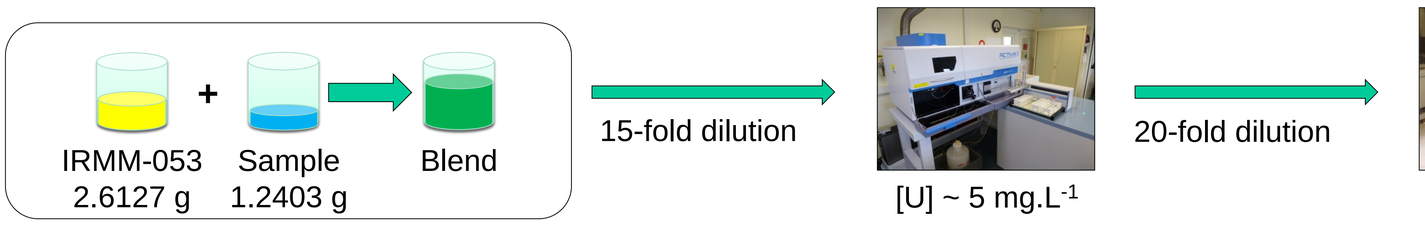
Isotopic dilution principle

$$C_S^{235_U} = C_{Sp}^{238_U} \times \frac{m_{Sp}}{m_S} \times \frac{1}{R_{Sp}} \times \frac{R_{Sp} - R_B}{R_B - R_S}$$

Isotopic dilution formula applied to determine amount content of ^{235}U ($C_S^{235_U}$) in the sample using a ^{238}U enriched CRM

*R*s= $n(^{238}U)/n(^{235}U)$ in the unknown sample, $R_{Sp} = n(^{238}U)/n(^{235}U)$ in the spike material, $R_B = n(^{238}U)/n(^{235}U)$ in the blend, m_S = weight of the unknown sample used to prepare the blend, m_{Sp} = weight of the spike solution used to prepare the blend, $C_{Sp}^{238_U}$ = amount content of ^{238}U per kilogram of spike solution.

The sample is a highly enriched uranium solution of the certified reference material SRM U-930 (U_3O_8 powder) in which the amount of ^{235}U is between 100 and 50 $\mu g.g^{-1}$. The spike (named IRMM-053) is an isotopic reference material certified for ^{238}U amount content (JRC IRMM, Geel, Belgium). The blend is prepared by mixing perfectly known weights of spike and sample.



Ratios of the blend are determined using the "Sample Standard Bracketing" method in order to correct instrumental bias (for ICP/AES and MC ICP/MS). The SSB method is based on an external correction. An isotopic reference material (SRM U-500) measured before and after the blend is used and the relative bias between the true and the experimental value is assumed to be valid for the blend as well. The ratio B is then equal to $R_B = R_B^{meas} \times \left(\frac{R_{std}^{True}}{R_{Std}^{meas}}\right)$

Instrument	R_B
ICP/AES	1.4945 ± 0.0460
MC ICP/MS	1.4955 ± 0.0022

$^{238}U/^{235}U$ of blend determined by ICP/AES and MC ICP/MS

Method	Amount content of ^{235}U in SRM U-930 sample ($mol.g^{-1}$)	Amount content of ^{235}U in SRM U-930 sample ($\mu g.g^{-1}$)
IDAES	$(3.081 \pm 0.099).10^{-7}$	72.42 ± 2.33
IDMS	$(3.079 \pm 0.007).10^{-7}$	72.37 ± 0.16

Amount content of ^{235}U determined by IDAES and IDMS

IDMS is the method of choice for quantification of an isotope or an element thanks to the accuracy and precision of the analysis. Although slightly less precise, IDAES clearly shows the accuracy of this method**. The difference between the amount contents of ^{235}U** determined by each method is **less than 0.1%**. This result is particularly notable since measurements are realised using two different physical measurements methods.

Conclusion

ICP-AES technique combined to isotopic dilution method (leading to IDAES) is fully appropriate for the determination of ^{235}U and/or ^{238}U concentrations, in terms of accuracy (trueness of the results) and precision. Indeed, results obtained thanks to this technique are quite similar to those given by MC ICP/MS (IDMS method) which is the preferred choice. This result is particularly remarkable because the physical principles of measurements of both instruments are different.

The highest precision of the IDMS method compared to the IDAES one is the result of the high precision of measurement of the MC ICP/MS. Nevertheless, this instrument is ten times more expensive than the ICP/AES one. The IDAES method is usable for physical follow-up and nuclear materials account.