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Introduction

An area of continuing intense interest has been the development of portable or fieldable (man-portable, luggable, or transportable) analytical instrumentation. One specific driver for portable or fieldable analytical instrumentation are the needs of the nuclear safeguards community for versatile, easy-to-use, in-field mass spectrometer systems for determining the $^{235}U/^{238}U$ isotope ratios in UF_6 at enrichment facilities. In order to meet this demand the authors propose using a liquid sampling-atmospheric pressure glow discharge (LS-APGD) ion source, Fig 1.[1-3] The LS-APGD was optimized for isotope ratio analysis to have a liquid flow rate of 30 uL min^{-1} a gas flow rate of 0.5 L min and a current of 30 mA. These operating parameters make the LS-APGD a promising ion source for infield mass spectrometry. In order to test the efficacy of the LS-APGD as an ion source capable of performing isotope analysis, it was interfaced with an Thermo Exactive Orbitrap mass spectrometer which was chosen for its atmospheric pressure inlet which is not available on commercial ICP-MS instruments. Due to the fact that there are no published studies using an orbitrap for isotope analysis, there are a large number of unknowns that need to be answered before the LS-APGD can be considered a viable option as an ion source for isotope analysis.

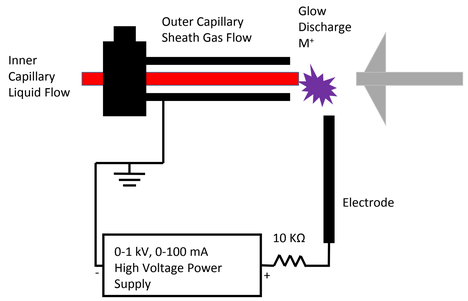

Fig. 1: Representative schematic of the proposed LS-APGD ion source

Collisional Dissociation to Simplify Spectral Complexity

The Exactive orbitrap has two options for removing interfering ions from being injected into the orbitrap detection cell; "in-source" collision-induced dissociation (CID) and the high-energy collisional dissociation (HCD) cell for CID with helium gas atoms. These two options were used as means of reducing undesirable background ions which add complexity to the spectra. Not only was the problem of interfering ions mitigated, there was no adverse effects on the signal for the U isotope signals.

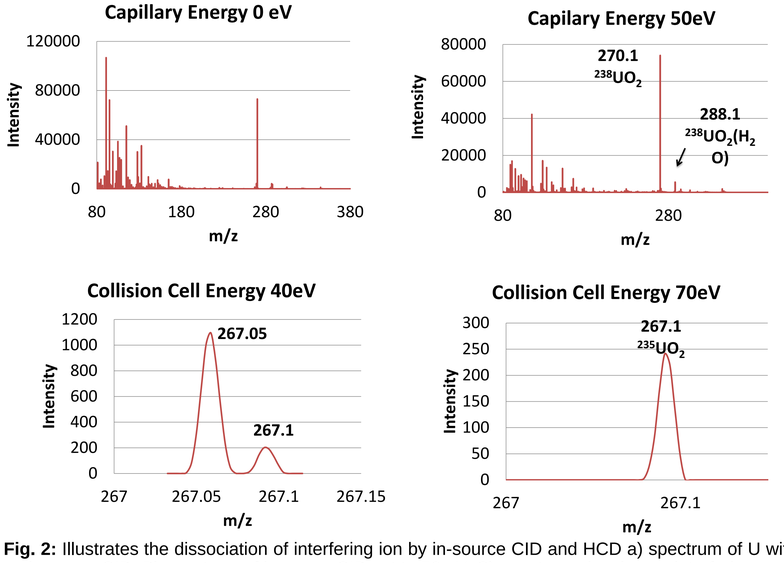

Fig. 2: Illustrates the dissociation of interfering ion by in-source CID and HCD a) spectrum of U with no insource CID. B) spectrum of insource CID set to 50 eV. C) spectrum showing an interfering peak at *m/z* 267 with a HCD set to 40 eV. D) spectrum showing only the ^{235}U signal without and interfering signals with the HCD set to 70 eV.

Fourier Transform Digitization Window

One of the common attributes of Fourier transform processing is the distribution of spectral noise across the entire spectrum which is counterproductive to the analysis of signals for ion with analytical relevance.[4] The orbitrap instrument available for these studies did not have the ability to conduct mass selection prior to injection into the orbitrap. This means that all of the ions above 50 Da that are generated by the ion source and that are not dissociated by CID are injected into the orbitrap which increases the complexity of the transient that is processed. This fact is demonstrated in Fig. 4a where the digitization window is seen to have a direct impact on the recorded isotope ratio for U (measured as the di-oxide ions). Fig. 4b shows the spectrum derived from processing a digitization window of 70 - 470 Da which is seen to have a large number of interfering ions. Fig. 4c shows a much narrower spectrum with a digitization window of 265 - 275 Da resulting in only the analyte of interest being processed.

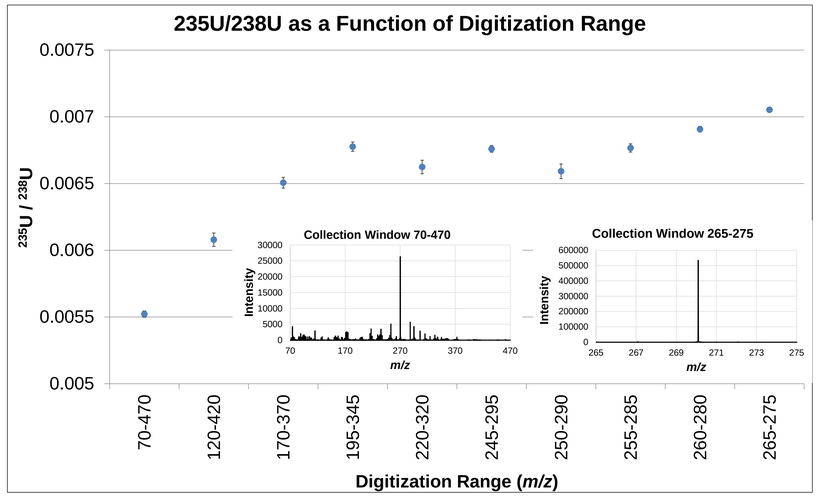

Fig. 3: shows the role of digitization window breadth on the product mass spectra for the equivalent mass ranges of a) 70 – 470 Da and b) 265 – 275 Da and c) the product $^{235}U/^{238}U$ ratios for 5 mg mL^{-1} solutions of uranyl nitrate.

Role of Automatic Noise Redution

A result of using the Xcalibur and Tune operating and data analysis software is the bias of the heavier ^{238}U isotope caused by automatic noise reduction that occurs. The automatic noise reduction works by removing all of the data under the gray bar seen in Fig. 5. While the noise is also removed from the ^{238}U signal (not shown), the effect it has on the 235U signal is proportionally greater leading to an isotope bias. This effect can be seen in Fig. 6 which shows the IR results of varying the solution concentration from 100 to 800 ng mL^{-1}. As the signal decreases as a result of decreasing concentration the automatic noise reduction plays a greater impact on the IR value.

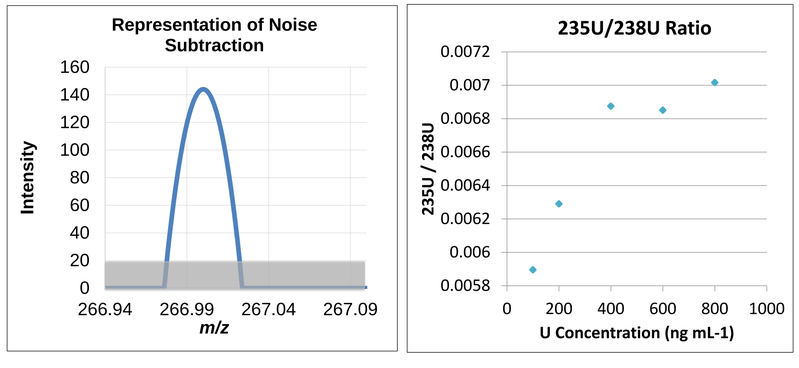

Fig. 4: Illustrates the effects of the automatic noise reduction on the isotope ratio. a) shows a representation of the spectrum as it is collected in the Xcalibur Software prior to the noise reduction which is represented by the grey bar. b) shows the isotope ratio results as a function of concentration after automatic noise reduction has occurred.

Uranium and Selected Element Results

Table 1: U Isotope ratio statistics for a depleted, a certified natural reference material and a certified enriched reference material. Results reflect 100 data points grouped by sets of 10. Each data point is made up of 50 scans of 10 microscans each.

	Depleted Sample $^{235}U/^{238}U$: 0.00192			Natural $^{235}U/^{238}U$: 0.007258 (certified CRM-129a)			Enriched Sample $^{235}U/^{238}U$: 0.03137 (certified U-030a)		
	^{235}U Fraction	^{238}U Fraction	^{235}U / ^{238}U	^{235}U Fraction	^{238}U Fraction	^{235}U / ^{238}U	^{235}U Fraction	^{238}U Fraction	^{235}U / ^{238}U
Average	0.00186347	0.99813653	0.001867	0.006829	0.993171	0.006865	0.029132	0.970868	0.030006
Standard Deviation	5.67E-05	5.67E-05	5.69E-05	8.60E-05	8.60E-05	9.37E-05	3.58E-04	3.58E-04	3.80E-04
%RSD	3.04	0.01	3.05	1.26	0.01	1.37	1.23	0.04	1.27

Table 2: Isotope ratio statistics for selected elements. Results reflect 10 data points made up of 50 scans of 10 microscans each.

Element	Isotope Ratio Measured	Natural Value	Measured Value	Standard Deviation	%RSD	Correction Factor
Ag	$^{109}Ag/^{107}Ag$	0.929	0.9520	3.88E-03	0.41	0.976
Rb	$^{87}Rb/^{85}Rb$	0.413	0.4206	2.20E-03	0.52	0.983
Tl	$^{203}Tl/^{205}Tl$	0.419	0.4169	3.27E-04	0.08	1.005
Pb	$^{204}Pb/^{208}Pb$	0.027	0.0236	7.80E-04	3.31	1.133
Pb	$^{206}Pb/^{208}Pb$	0.46	0.4752	1.01E-03	0.21	0.968
Pb	$^{207}Pb/^{208}Pb$	0.422	0.3971	6.27E-04	0.16	1.062
Ba	$^{130}Ba/^{138}Ba$	0.001	0.0010	1.56E-05	1.57	1.4214
Ba	$^{132}Ba/^{138}Ba$	0.001	0.0010	1.37E-05	1.37	1.3556
Ba	$^{134}Ba/^{138}Ba$	0.034	0.0308	1.10E-04	0.36	1.0968
Ba	$^{135}Ba/^{138}Ba$	0.092	0.0889	2.60E-04	0.29	1.035
Ba	$^{136}Ba/^{138}Ba$	0.109	0.1066	6.75E-04	0.63	1.0223
Ba	$^{137}Ba/^{138}Ba$	0.158	0.1539	7.29E-04	0.47	1.0264
Ce	$^{136}Ce/^{140}Ce$	0.002	0.0016	3.62E-05	2.30	1.3635
Ce	$^{138}Ce/^{140}Ce$	0.003	0.0023	3.86E-05	1.71	1.3033
Ce	$^{142}Ce/^{140}Ce$	0.125	0.1262	6.42E-04	0.51	0.9937

Conclusions

For a proof of concept system, the LS-APGD interfaced with an orbitrap mass analyzer showed promising results. The key aspects of LS-APGD operation to yield sensitive mass spectroscopic element and isotope analysis were confirmed. Of greater relevance was the work completed to determine the operating parameters that resulted in lower amounts of spectral noise to increase the accuracy of isotope measurements on an orbitrap mass analyzer. The quantitative results presented in Tables 1 and 2 are encouraging for the use of the LS-APGD as an ion source for field-deployable isotopic analysis. Moving forward, a greater understanding of the background subtraction methods and Fourier transform processing is required. As these unknowns are answered, focus can turn to any limitations imposed by the LS-APGD as an ion source for isotope analysis

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