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2 **for uranium optical isotopic analysis**
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21 **Abstract**

22 Through computer simulation on experimentally acquired optical spectra, uranium
23 isotopic analysis by laser ablation molecular isotopic spectrometry (LAMIS) and laser
24 induced breakdown spectroscopy (LIBS) were studied. The use of only one spectral
25 feature, either the strong UO band at 593.55 nm or the nearby U I 593.382 nm line, are
26 similar in precisions (~1.5% in absolute ^{235}U abundances). Precision improves to 0.72%
27 with the use of a group of U atomic lines from 591.6 to 596.5 nm. The use of both
28 molecular bands and atomic lines further advances the precision to 0.42% and compares
29 well with the U II 424.437 nm single-line benchmark (0.48% precision).

30 **Keywords**

31 Optical isotopic analysis; Uranium; Laser ablation molecular isotopic spectrometry;
32 Laser induced breakdown spectroscopy; Isotope shift.

33 **Introduction**

34 The capability to perform direct chemical analysis on any solid sample is one of the
35 distinguishing characteristics of laser-ablation based analysis. Chemical information
36 (both elemental and isotopic) of the sample is contained in the light emitted by the laser-
37 induced plasma and can be readily probed with an optical spectrometer. The technique
38 termed laser induced breakdown spectroscopy (LIBS) involves the measurement of
39 photon emission typically from atoms (i.e., atomic emission spectrometry); in this
40 particular context, the atom can be either charged (i.e., ionized) or as neutral. In contrast,
41 laser ablation molecular isotopic spectrometry (LAMIS) measures the spectra from
42 molecular radicals that are present when the plasma cools. These two spectrometric
43 techniques are very similar in implementation; in fact, they are produced by and can be
44 measured from the same laser pulse.

45 The choice of utilizing atomic (i.e., LIBS) or molecular (i.e., LAMIS) spectra for a
46 measurement depends on the application. In general, LIBS is used to determine the
47 content of a particular element of interest in the sample (i.e., elemental analysis) whereas
48 LAMIS is employed to evaluate isotopic ratio of a particular element (i.e., isotopic
49 analysis). This simple classification is based on the fact that an atom (or an atomic ion)
50 possesses only electronic energy levels. Isotopic shifts in electronic energy levels (except
51 the very light and heavy elements) are generally too small to be measured inside
52 atmospheric-pressure plasma, in which several line broadening mechanisms are
53 operating. In contrast, because the vibrational and rotational motions of a molecule
54 heavily depend on its reduced mass, the additional vibrational and rotational energy
55 levels in a molecule greatly amplify the isotopic effects on optical spectra. Consequently,
56 isotopic shifts exhibited in molecular spectra may exceed those in atomic spectra by two
57 to three orders of magnitude [1-3], and become readily measurable in an atmospheric-
58 pressure plasma. Isotopic LAMIS signatures from a number of elements, including H, B,
59 C, N, O, Sr and Zr [1-6], have already been reported.

60 For the very light or heavy elements, LIBS (atomic spectra) can also be used for their
61 isotopic measurements. For light elements, the different masses of isotopes cause a
62 relatively large fractional change in the mass of the atom, which in turn alters the electron
63 motion with respect to the center of gravity of the atoms and hence the associated
64 electronic energy levels. This mass effect is the largest for hydrogen. For instance, the
65 H α and H β lines at 656.464 nm and 486.270 nm are shifted by -174 pm and -130 pm,
66 respectively, for deuterium [7]. For heavy atoms, the large nucleus modifies the
67 electronic energy level of the atom through interactions between the shape and the size of
68 the nuclear charge distribution with the field of the electrons [8, 9]. This field effect is
69 strongest for those electrons that have a finite probability at the origin of the nucleus (i.e.,
70 s-electrons) [9]. Accordingly, atomic lines of heavy elements (e.g., U) also exhibit
71 appreciable isotope shifts, which can reach tens of picometers [10-12].

72 Several researchers have reported hydrogen-deuterium analysis by means of LIBS
73 operated under atmospheric pressure [4, 13-16]. Cremers *et al.* [13] also performed
74 isotopic analysis on ^6Li and ^7Li with LIBS under atmospheric pressure. For heavy
75 elements, uranium has been mostly studied [13, 14, 17, 18]. Doucet *et al.* [14] reported
76 the first study of uranium isotopic analysis with atmospheric pressure LIBS. Although
77 the atomic lines from the two uranium isotopic components were only partially resolved,
78 they demonstrated that isotope ratios can be accurately extracted from the spectra through
79 the use of chemometrics. Cremers *et al.* [13] utilized a spectrometer with a resolution of
80 75,000, and reported baseline separated isotopic components for the U II 424.437 nm line
81 in atmospheric pressure LIBS. Recently, Morgan *et al.* [17] developed and applied a
82 hybrid interferometric/dispersive spectrometer to measure laser-induced plasma from a
83 metallic uranium foil, and reported that the ^{235}U - ^{238}U isotope shift at U II 424.437 nm
84 was resolved in ambient air. We previously performed uranium isotopic analysis in soil
85 matrix with atmospheric-pressure LIBS, and compared the effectiveness of several fitting
86 algorithms to extract isotopic information from the LIBS atomic spectra [18]. LIBS also
87 has been applied to the determination of ^{239}Pu / ^{240}Pu isotopic ratios [19], albeit at a
88 reduced pressure of 13.3 kPa.

89 As LAMIS is a relatively new technique, many of its analytical characteristics have not
90 yet been established. There are three objectives in the present study. Currently, the
91 heaviest element measured with LAMIS for isotopic analysis is Zr ($Z = 40$) [5, 20].
92 Therefore, the first objective of the present study is to investigate the isotopic spectral
93 features and signal characteristics when LAMIS is applied to a very heavy element like
94 uranium ($Z = 92$). Second, for those elements whose isotopic ratios can be determined
95 with either LIBS or LAMIS, the advantage of one technique over another is largely
96 unknown. So far, there is only one study [4] that compared LIBS and LAMIS side-by-
97 side for isotopic analysis. Sarkar *et al.* [4] assessed both techniques for
98 deuterium/protium ($^2\text{D}/^1\text{H}$) isotopic ratio determination. The $\text{H}\alpha$ and $\text{D}\alpha$ atomic lines
99 were used for LIBS whereas the OH and OD $A^2\Sigma^+ - X^2\Pi$ molecular bands were utilized
100 for LAMIS [4]. It was concluded that the analytical performances of LAMIS was
101 superior to LIBS for isotopic analysis of hydrogen [4]. Specifically, LAMIS provided an
102 accuracy of 0.5-1.5% compared to 2-5% for LIBS [4]. Although almost all atomic
103 emission lines are broadened by Stark effects inside laser induced plasmas, Stark
104 broadening is particularly pronounced for hydrogen as it is a first-order effect for
105 hydrogen but only second order for other non-hydrogenic atoms [21]. For instance, in the
106 aforementioned LIBS work, the reported line width (full width at half maximum,
107 FWHM) of the $\text{H}\alpha$ atomic line at a gate delay of 10 μs was still 350 pm and was nearly
108 double that of the isotopic shift [4]. However, spectral characteristics for uranium are
109 dramatically different, and it is currently unknown how LAMIS compares with LIBS for
110 isotopic analysis of uranium. Therefore, the second objective of the present work is to
111 assess and compare LAMIS and LIBS for isotopic analysis of uranium. Further, as will
112 be discussed below, emission from U atomic lines and UO molecular bands strongly
113 overlap in time, and spectra acquired at appropriate delay times contain both LIBS and
114 LAMIS signals for U. Understanding the potential of including molecular bands with
115 atomic lines (i.e., a combined LAMIS–LIBS approach) for U isotopic analysis is the third
116 objective of the present study.

117 Similar to our previous studies [10, 22], experimentally determined measurement
118 characteristics, including noise amplitude and distribution, signal strength, and signal-to-

119 background ratio were incorporated into the simulation model. The ^{235}U and ^{238}U
120 LAMIS–LIBS spectral profiles used in the simulation were also determined
121 experimentally. It should be stressed that, as the simulation does not include all sources
122 of uncertainties and factors that are present in a real analysis, the analytical figure of
123 merit from simulation represents only the theoretical limit under an idealized situation,
124 and does not reflect what can be typically achieved in routine analyses. Nevertheless,
125 computer simulation is adequate to satisfactorily provide a relative comparison of the
126 effectiveness of different spectral features (single atomic line, multiple atomic lines,
127 single molecular band, all measured spectral lines and bands) for isotopic analysis of
128 uranium, which is one of the main themes of the present paper.

129 **Experimental**

130 **Sample and experimental setup**

131 Two sample pellets made from certified U_3O_8 powder (New Brunswick Laboratory, US
132 Department of Energy) with enriched (63.35% ^{235}U , CRM U630) and depleted (0.02%
133 ^{235}U , CRM U0002) uranium isotopes were prepared by pressing about 15 mg of the
134 powder with a 3-mm diameter pellet-pressing die. The U_3O_8 pellets, which were about
135 300 μm thick, were loaded into a shielded chamber, which contained air at atmospheric
136 pressure, with optical ports for laser ablation and photon collection. Ignoring trace
137 amount of other uranium minor isotopes (i.e., assuming ^{235}U and ^{238}U sum to 100% of all
138 uranium atoms in the CRM), the ratio of $^{235}\text{U}:^{238}\text{U}$ in the enriched sample is 64.4:35.6.

139 The experimental setup consisted of a nanosecond Nd:YAG laser operated at its
140 fundamental wavelength at 1064 nm, a 1.25 m-focal length Czerny-Turner spectrometer
141 (Horiba JY 1250M), and an intensified charge-coupled device (ICCD) gated detector
142 [23]. A pulsed laser, with energy of 40 mJ, was focused onto the sample surface with a
143 fused-silica lens to a spot diameter of approximately 400 μm . Laser-induced plasma
144 emission was collected through another fused-silica lens onto an optical fiber bundle
145 coupled to the spectrometer. Unless otherwise specified, a grating with a groove density

146 of 2400 lines per mm was used (measured spectral resolution was ~ 18 pm FWHM); the
147 delay time and gate width of the ICCD detector were set at 5 μ s and 20 μ s, respectively.

148 Simulation of LIBS and LAMIS spectra

149 Because databases for spectroscopic constants and isotopic shifts are adequately
150 comprehensive for U atomic lines (U I and U II [11, 12, 24]) but those for molecular UO
151 [25-27] are far from complete, the methods for generating simulated spectra were
152 accordingly different for atomic lines and molecular bands. For simulations involving
153 only atomic emission lines, the simulated spectra were all based on theoretical
154 computation. Published wavelengths from the ^{238}U line list [24] were directly taken for
155 the simulation of the ^{238}U profile, and line positions for the ^{235}U isotope were calculated
156 from the published isotopic shifts [11, 12]. Lorentzian line profiles, with a measured
157 width of 18 pm for emission lines in the 590 nm proximity, were used for the
158 computation of atomic spectra. For the U II 424.437 nm line, a spectral width of 15 pm
159 was used in the simulation because this line can be measured with a 3600 groves/mm
160 grating, in which the cutoff wavelength is 500 nm.

161 For molecular bands, as will be explained in detail in Section 3.1, the persistence time for
162 UO molecular bands and U atomic lines overlap. In other words, LAMIS spectra for UO
163 bands unavoidably contain some U atomic lines. Since these U lines contain isotopic
164 information of the sample and are inherently present in the LAMIS spectra, a combined
165 LAMIS–LIBS approach was used for isotopic analysis. For the simulation, a set of ^{235}U
166 and ^{238}U base LAMIS–LIBS spectra were obtained from experiments. Because more
167 than 99.98% of uranium in the depleted U_3O_8 sample (CRM U0002) is in the form of
168 ^{238}U , the ^{238}U LAMIS–LIBS base spectrum is taken directly from this depleted U_3O_8
169 sample. As will be discussed in detail in Section 3.2, the ^{235}U LAMIS–LIBS base
170 spectrum is deduced from the difference between the depleted and enriched (CRM U630)
171 U_3O_8 samples. Once the ^{235}U and ^{238}U base LAMIS–LIBS spectra are determined,
172 simulation of uranium emission spectra at any desired ^{235}U and ^{238}U abundance

173 percentages becomes straightforward through summation of the two U isotopic
174 components.

175 In all cases, emission intensities, signal-to-background ratios, and measurement noise
176 (detector-read, photon-shot and source-flicker) were all experimentally determined and
177 incorporated into the simulation model [10, 22]. For the two U₃O₈ pelletized samples,
178 the measured pulse-to-pulse flicker noise was 14.8% RSD. As the same spectrometric
179 and detector system was used as in our earlier work [10], the previously determined
180 distributions of detector-noise and photon-shot noise were applied in the present study.
181 The detector-read, photon-shot and source-flicker noise levels were independently added
182 to all simulated spectra.

183 Partial least square regression

184 Extraction of isotopic abundance information from the LIBS or LAMIS spectra was
185 achieved with partial least square (PLS) multivariate regression [10, 22]. As PLS
186 regression is a purely empirical approach by matching the emission pattern of the sample
187 with unknown ²³⁵U/²³⁸U ratio to a set of standard reference spectra; it is particularly
188 useful in uranium LAMIS analysis because spectroscopic constants of many rovibronic
189 bands for UO are not documented. In addition, even when the two U isotopic
190 components in the measured spectra are overlapped and resolved only partially, PLS
191 multivariate calibration can be correctly performed [28, 29].

192 In this work, with the exception of the two base spectra from experimental measurements
193 (Section 3.2), all other standards and samples spectra were simulated from these two base
194 profiles. However, the signal and noise behaviors in these simulated spectra should
195 resemble those obtained from experiments, as several noise sources were individually
196 characterized in detail. For ease of discussion and to match typical terminology as in an
197 analysis, from this point onwards, the fact that all spectra of the samples and the
198 standards were simulated will no-longer be repeatedly stressed.

199 The calibration set consisted of eleven standards with equally spaced ^{235}U abundances
200 from 0% to 100%, whereas the test set contained ten reference samples with ^{235}U
201 abundances evenly distributed between 5% and 95%. The spectra from both the
202 calibration standards and the test samples were each accumulated from 10 laser shots.
203 For each standard, ten replicated spectra were fed into the PLS calibration model. For
204 each test sample, 1000 repeated measurements were made. Assessment of standard
205 deviation requires a large number of samples to be measured, and we have previously
206 [10] shown that 1000 to 3000 measurements is a good compromise between being able to
207 confidently estimate the measurement precision and computation time.

208 Prior to feeding the spectra into the PLS algorithm, all individual emission spectra were
209 normalized to its norm [29, 30] as a data pre-processing routine to reduce systematic
210 variation and minimize the spectrum uncertainty [29, 31-33]. All spectra simulation and
211 PLS analyses were performed with in-house written LabVIEW programs (LabVIEW
212 2015, National Instruments). The PLS algorithm used in this study was a PLS1 type and
213 three principal components were utilized in all PLS calibration models [22].

214 **Results and discussion**

215 Identification of U atomic and molecular spectral features

216 Laser induced plasma emission from uranium is complex in structure as uranium gives
217 rich, and in many cases overlapping, atomic and molecular spectra. For instance, 92,000
218 U I and U II lines have been observed and were compiled between the wavelength range
219 of 310 to 900 nm [11], which translates to an average of one atomic line in each 6.4-pm
220 spectral window. The UO molecular spectra are even more complex with an average of
221 one molecular *band* in a 1-nm spectral window in the UV-visible range. Kaledin *et al.*
222 [34] reported that approximately 500 UO molecular bands were observed in the emission
223 spectrum in the 400 to 900 nm range with a thermal furnace excitation source operated at
224 2400 to 2600 K. Although a large number of UO molecular bands have been detected,
225 only a small fraction of those were characterized. The most extensive list on UO

226 rovibronic levels currently available was published by Kaledin and Heaven [26]; yet,
227 only about fifty UO levels were listed.

228 A spectral window that contains a strong UO molecular band is selected for this work.
229 Several studies, both experimental [35, 36] and theoretical [27], reported that the most
230 intense UO band is the one that emits at 593.4 nm. Furthermore, it was commented that
231 overlapping of UO bands are particularly marked in the range of 580 to 610 nm [34].
232 Because PLS regression extracts isotopic information through matching the emission
233 pattern of the sample and the calibration standard, and requires the molecular bands to be
234 resolved only to an extent that there are differences in the spectral features from the two
235 isotopologues, heavily overlapping spectral features could be beneficial as they contain a
236 high density of information. Therefore, the spectral window from 591.6 to 596.5 nm was
237 chosen for the present study. As will be presented below, thirty-two U I lines and three
238 UO bands were positively identified in this comparatively narrow spectral window that
239 spans slightly less than 5 nm.

240 Emission features from atomic lines or molecular bands can be readily classified through
241 temporally resolved spectra. Figure 1 shows a small section of the measured emission
242 spectra, normalized to the gate width of the ICCD detector, at different delay times, from
243 laser ablation of a depleted U_3O_8 pellet sample. Ionic emission lines (e.g., U II
244 593.244 and U II 595.205) are strong at early times of the plasma (e.g., 1 μ s) but then
245 rapidly decrease to almost baseline level at 5 μ s. Neutral-atomic lines (e.g., U I 592.933,
246 U I 593.382, and U I 594.277) resemble ionic lines and show strong emission at early
247 delay times (<1 μ s). The major difference is that neutral-atomic lines persist significantly
248 longer, and is one of the two major emitting species at 5 μ s delay. Molecular bands (e.g.,
249 the UO bands at 593.55, 594.57 and 595.22 nm), in contrast, are relatively weak at early
250 times (<1 μ s), but progressively grow and become comparatively strong at longer delay.
251 For example, emission from the UO band at 593.55 nm is only a small fraction to that of
252 the nearby U I 593.382 nm line at 1 μ s; the UO band/U I line ratios gradually increase
253 with delay time, and the UO band becomes stronger than the U I line at 5 μ s. Temporally

254 resolved study, as demonstrated in Fig. 1, allows the classification of emission features
255 even for spectra as complex as uranium.

256 Figure 1 also illustrates two spectral characteristics that would potentially pose impacts
257 on isotopic analysis of uranium by LIBS/LAMIS. First, emission from UO molecular
258 bands and U atomic lines temporally overlap, and it is not practically feasible to select a
259 delay time and detection gate that can measure strong emission from UO bands without
260 U I lines (and vice versa). Therefore, there will be no clear boundary on LIBS (atomic
261 line only) and LAMIS (molecular band only) for U isotopic analysis in laser induced
262 plasmas. Indeed, it is one objective of the present study to understand the potential
263 benefit of including molecular bands to atomic lines for U isotopic analysis. Second, the
264 temporal response of the plasma background appears atypical. Rather than following a
265 monotonically decreasing trend [37], the plasma background initially dropped when the
266 delay time was increased from 1 μ s to 2 μ s, but then rose at 3 μ s and further grew at 5 μ s.
267 This rising trend for plasma background at 3 and 5 μ s is a result of a pseudo-continuum
268 from the strongly overlapping UO molecular bands. Previous studies [38, 39] also noted
269 intense plasma continuum from a superposition of a multitude of uranium emitting
270 species during laser ablation of metallic uranium samples. An intense pseudo-continuum
271 degrades signal-to-background ratio, and analytical performance could suffer.

272 Determination of LAMIS–LIBS base spectra for ^{235}U and ^{238}U

273 For the simulation, a set of ^{235}U and ^{238}U base LAMIS–LIBS spectra were obtained from
274 experiments. Because the two (depleted and enriched) U_3O_8 samples are in the form of
275 pressed pellet housed in separate air-tight chambers, the measured total emission from the
276 two samples was slightly different, probably due to the small variations in the sample
277 properties (e.g., particle size distribution, density and thickness of the pressed pellet) and
278 the reproducibility in positioning the two chambers. Further, our enriched sample
279 contains only $\sim 64\%$ ^{235}U . Therefore, a simple model was developed to deduce the base
280 spectrum for 100% ^{235}U from the depleted and enriched U_3O_8 samples, as well as to
281 correct for the slight mismatch in the measured intensities.

282 The measured spectrum from an U_3O_8 sample (denoted as $I^{measured}(\lambda)$) contains two
283 components – emission from both atomic and molecular species of uranium with the
284 associated pseudo-continuum ($\varepsilon_U(\lambda)$), and true plasma continuum background solely due
285 to ion-electron (either free-free or free-bound) recombination ($\varepsilon_{bkg\text{-continuum}}(\lambda)$).

$$I^{measured}(\lambda) = \varepsilon_U(\lambda) + \varepsilon_{bkg\text{-continuum}}(\lambda) \quad (1)$$

286 It is clear that the U-emission component ($\varepsilon_U(\lambda)$) in the measured spectrum is related to
287 the amount of uranium ablated and present in the plasma (N_U); a U-density normalized
288 emission-signal coefficient ($S_U(\lambda)$), is defined *via* the relation:

$$\varepsilon_U(\lambda) = N_U S_U(\lambda) \quad (2)$$

289 It is difficult to model the true plasma continuum background component ($\varepsilon_{bkg\text{-continuum}}(\lambda)$)
290 as it involves number densities of ions, electrons and their kinetic temperatures. For the
291 present measurements, the delay time was 5 μs after the laser pulse and the densities of
292 electrons and ions are expected to be low. Hence, the plasma continuum due to ion-
293 electron recombination should be significantly decayed [2, 37]. For example, using a
294 similar setup with an uraninite ore sample but at other wavelengths, we previously
295 reported that the intense plasma continuum emission undergoes rapid decay at 1 μs delay
296 [23]. Although it is expected that the contribution of $\varepsilon_{bkg\text{-continuum}}$ to the total emission is
297 minor, it is included in the derivation of the base profile. Justified by the fact that plasma
298 continuum has been successfully employed as an internal standard for LIBS [40, 41], it
299 can be assumed that $\varepsilon_{bkg\text{-continuum}}$ is directly proportional to N_u (the amount of uranium
300 ablated and present in the plasma) through the U-density normalized background
301 coefficient ($B_U(\lambda)$). Furthermore, we assume that this normalized background coefficient
302 ($B_U(\lambda)$) is identical for ^{235}U and ^{238}U in the laser plasma.

$$\varepsilon_{bkg\text{-continuum}}(\lambda) = N_U B_U(\lambda) \quad (3)$$

303 The experimentally measured emission spectrum (Equation 1) can be re-written as

$$I^{measured}(\lambda) = N_U(S_U(\lambda) + B_U(\lambda)) \quad (4)$$

304 The term $(S_U(\lambda) + B_U(\lambda))$ represents the base spectrum, which is the spectrum normalized
 305 to the amount of ablated material in the plasma. The base spectrum can be conveniently
 306 obtained through normalization of the measured spectrum with its total intensity (i.e.,
 307 area under the spectrum). The normalization effectively compensates the slight mismatch
 308 in ablation efficiencies of the two samples. Because more than 99.98% of the uranium is
 309 in the form of ^{238}U in the depleted U_3O_8 sample, the base spectrum for ^{238}U , $(S_{U-238} + B_U)$,
 310 is simply the measured spectrum from the depleted sample after normalization with its
 311 total intensity.

$$(S_{U-238}(\lambda) + B_U(\lambda)) = \frac{I_{depleted-U}^{measured}(\lambda)}{\sum I_{depleted-U}^{measured}(\lambda)} \quad (5)$$

312 The procedure to obtain the base spectrum for ^{235}U , $(S_{U-235} + B_U)$, is slightly more
 313 complicated because the $^{235}\text{U}:^{238}\text{U}$ ratio in the enriched U_3O_8 sample is only 64.4:35.6.
 314 Measured emission for the enriched sample, therefore, is

$$\begin{aligned} I_{enriched-U}^{measured}(\lambda) &= N_{enriched-U}(S_{enriched-U}(\lambda) + B_U(\lambda)) \\ &= N_{enriched-U}[0.64(S_{U-235}(\lambda) + B_U(\lambda)) \\ &\quad + 0.36(S_{U-238}(\lambda) + B_U(\lambda))] \end{aligned} \quad (6)$$

315 After rearrangement and with Equation 5, the base spectrum for ^{235}U , $(S_{U-235} + B_U)$, can
 316 be obtained from the total intensity-normalized spectrum of the enriched and depleted
 317 sample through

$$\begin{aligned} (S_{U-235}(\lambda) + B_U(\lambda)) &= \frac{1}{0.64} \left[\frac{I_{enriched-U}^{measured}(\lambda)}{\sum I_{enriched-U}^{measured}(\lambda)} - 0.36(S_{U-238}(\lambda) + B_U(\lambda)) \right] \\ &= \frac{1}{0.64} \left[\frac{I_{enriched-U}^{measured}(\lambda)}{\sum I_{enriched-U}^{measured}(\lambda)} - 0.36 \frac{I_{depleted-U}^{measured}(\lambda)}{\sum I_{depleted-U}^{measured}(\lambda)} \right] \end{aligned} \quad (7)$$

318 With Equations 5 and 7, base profiles for both ^{235}U and ^{238}U were obtained from the
 319 measured spectra of the enriched and depleted U samples. Several atomic lines and

320 molecular bands were found to exhibit distinct isotope shifts, and some of these spectral
321 features are presented in Figs. 2a and 2b.

322 The strongest UO band at 593.55 nm with its neighboring U I line at 593.382 nm are
323 shown in Fig. 2a. In this manuscript, all wavelengths are referenced to the ^{238}U isotope.
324 The ^{235}U isotope shift for the U I line is +8.5 pm (i.e., towards the red) whereas the shift
325 for the peak of the UO band is ~ -35 pm (i.e., a blue shift). The isotopic shift for the UO
326 band is only a few times larger than that of the U I line, partly due to the exceptionally
327 large isotopic shift for U atomic lines as mentioned in the introduction, and partly
328 because the reduced mass of UO molecule is dominated by the much lighter O atom and
329 hence is only slightly altered when the U atom is changed from ^{238}U to ^{235}U . Based
330 solely on the magnitude of its isotope shift, the UO band might not look particularly
331 attractive for isotopic analysis. However, the substantial perturbations in the UO
332 molecular energy levels [36, 42] provide some additional unique spectral features that
333 can be exploited for isotopic analysis. To elaborate, because of the large number of
334 electronic states available and the high degree of configuration mixing present in
335 uranium, perturbations in U-bearing molecular energy levels are heavy and frequent [42-
336 44]. Heaven *et al.* [42] and Kaledin *et al.* [25, 26] found that many UO bands are
337 perturbed to a degree that prevented rotational analysis. Because the extent of
338 perturbations depends on the specific interactions and mixing of the energy levels, which
339 is isotope dependent, it has been reported that perturbations in UO are different for its
340 isotopologues [43] and the effect of isotopic substitution on the spectrum is so profound
341 that the correlation between bands for the two species cannot be made with any
342 confidence [42]. These isotope-specific perturbations in UO bring not only abnormally
343 large isotopic shifts than those predicted from a classical reduced-mass formula in
344 molecular spectroscopy, but also change the spectral intensity and pattern [42]. For
345 example, Heaven *et al.* [42] reported that U^{16}O has only one intense feature in the 17450–
346 17700 cm^{-1} spectral region but U^{18}O shows two strong features in this region with
347 intensities differing by a factor of six. The dramatic change in spectral pattern by
348 isotopic substitution in UO provides a beneficial feature for isotopic analysis.

349 Figure 2b shows a small section of the LIBS and LAMIS spectra from 594.25 to
350 595.25 nm for ^{235}U and ^{238}U . In this 1-nm spectral window, six U I lines and two UO
351 bands were identified. The wavelengths of the two identified UO bands match those
352 listed by Kaledin and Heaven [26]. Both UO bands exhibit dissimilar spectral patterns
353 for the two isotopologues, and their differences are more than merely simple wavelength
354 shifts. These differences can be readily extracted by the PLS regression calibration and
355 utilized for isotopic analysis.

356 Simulation of U isotopic analysis by LAMIS with only one UO band at
357 593.55 nm

358 To simulate the analytical performance of LAMIS with a single UO molecular band, the
359 most intense band at 593.55 nm was chosen. The simulation was comprised of isotopic
360 determination of ten simulated reference samples with ^{235}U abundances evenly
361 distributed between 5% and 95%. Spectral features from 593.424 to 593.849 nm in the
362 experimentally determined spectra (cf. the marked region in Fig. 2a) were used as base
363 profiles for this single-band LAMIS simulation. Figure 3 shows the difference between
364 predicted and true values (left axis) and predicted ^{235}U isotopic abundances (right axis)
365 against the ^{235}U isotopic abundances in the sample. Because the calibration standards and
366 the samples in the simulation model were obtained through *linear* combinations of the
367 two ^{235}U and ^{238}U base profiles, the addition of noise affects only precision and no bias is
368 expected from the PLS model (cf. Fig. 3). The absolute precisions were about 1.5% for
369 all studied ^{235}U abundances. Furthermore, in simulations with other spectral features
370 (e.g., single atomic line, pool of multiple atomic lines, combined LAMIS–LIBS) to be
371 discussed below, it was found that all precisions were independent of the ^{235}U
372 abundances. Therefore, it is a more straightforward approach to evaluate and compare
373 the performance through averaged precision of all the test samples, which is defined as
374 $\sqrt{\frac{1}{N} \sum (C_{pred} - C_{true})^2}$. Because there is no expected bias, the differences between the
375 predicted (denoted by C_{pred}) and the standard (C_{true}) isotopic abundances reflect only
376 precision. The averaged precision of all the ten test samples presented in Fig. 3 is 1.49%
377 in absolute ^{235}U abundances.

378 Simulation of U isotopic analysis by LIBS with U lines in-between 591.6
379 and 596.5 nm

380 The analytical performances of pure U atomic lines (i.e., without contributions from
381 molecular bands) in the spectral window from 591.6 to 596.5 nm also were simulated.
382 The results were compared to those with the contributions from molecular bands in the
383 same spectral window to be presented in the next section. Unlike the case with molecular
384 band, in which base spectra for ^{235}U and ^{238}U were obtained experimentally (cf. Figs. 2a
385 and 2b), simulated emission spectra for *pure* atomic lines were theoretically computed
386 from a published line list [24] and isotopic shifts [11] to ensure that the simulation results
387 represent the case when only atomic-line spectral features are used in the isotopic
388 analysis.

389 If the analysis is limited to a single atomic line, the strongest emission line should be
390 used providing that its isotopic shift is adequate. Our previous results [10] showed that
391 the quality of isotopic analyses of U by LIBS generally are dependent on the signal-to-
392 background ratio (SBR) and net intensity of the emission line, rather than the magnitude
393 of isotopic shifts. Accordingly, the strongest U I line at 593.382 nm was selected for
394 single-line analysis (cf. Fig. 2a). The experimentally measured SBR for this U I line was
395 0.43. The averaged simulated precision from the ten test samples is 1.62% in absolute
396 ^{235}U abundances, which is only slightly degraded from the case of a single UO band. The
397 SBRs of the U I 593.382 nm line and the UO 593.55 nm band are very similar
398 (cf. Fig. 2a) whereas their isotopic shifts are 8.5 pm and 35 pm, respectively; yet, their
399 simulated precisions are very comparable, which is in agreement with our previous
400 findings [10].

401 The simulation was further extended to multiple atomic-line analysis. All U I lines
402 between 591.6 and 596.5 nm documented in the extensive line list by Palmer *et al.* [24]
403 were included. This spectral window matches that captured by a single ICCD exposure
404 with our spectrometer-detector system. Emission intensities reported by Palmer *et al.*
405 [24] were from a hollow cathode discharge with an electronic excitation temperature

406 around 4400 K, and can be readily transformed to other temperatures (e.g., the
407 temperature of our LIBS plasma). Table 1 lists the spectroscopic constants [45] of the
408 three U I lines used to determine the excitation temperature of our LIBS plasma. Linear
409 regression (with $R^2 > 0.98$) of the Boltzmann plot gave an excitation temperature of
410 5300 K. The uncertainty in the slope of the Boltzmann plot was 10%. Table 2 lists the
411 wavelengths, ^{235}U – ^{238}U isotope shifts, upper energy levels, and rescaled relative
412 intensities to a temperature of 5300 K of the thirty-two U I lines used in the multiple-line
413 simulation. Figure 4 shows the experimentally measured ^{238}U LAMIS–LIBS (molecular
414 bands together with atomic lines) spectrum and the simulated U I lines (before addition of
415 plasma continuum background and simulated measurement noise). Overall, the pattern
416 of the simulated U I lines matches well with those from measurement. Those spectral
417 features in the LAMIS–LIBS experimental spectrum that are not covered by the
418 simulated U I profile likely originate from UO molecular bands.

419 In this multiple atomic-line simulation, the SBR of the U I 593.382 nm line was kept 0.43
420 (i.e., identical to the single line case) and emission of other U I lines were then varied
421 according to the predefined relative intensities listed in Table 2. The use of multiple
422 emission lines brings a significant improvement in the analytical performance compared
423 to the use of single atomic line or UO band. The averaged precision from the ten test
424 samples lowers to 0.72%.

425 Simulation of U isotopic analysis by LAMIS–LIBS combined approach

426 As mentioned earlier, there are temporal overlaps in the UO molecular bands and U
427 atomic lines. These spectral features (LAMIS and LIBS) can be used together for the
428 isotopic analysis. Experimentally measured LAMIS–LIBS base profiles for ^{235}U and
429 ^{238}U (cf. Figs. 2a and 2b), were used in the simulation. The spectral window was the
430 same as in the case of multiple atomic lines simulation (i.e., between 591.6 and
431 596.5 nm). Figure 5 summarizes the averaged precision of ^{235}U isotopic abundance for
432 different combinations of spectral features incorporated into the analysis. Compared to
433 the use of only atomic lines (LIBS with a collection of multiple lines), the inclusion of

434 multiple UO molecular bands in the analysis further improve the precision from 0.72% to
435 0.42%. These results clearly show that although many of the molecular features are faint
436 and appear noisy (many of them are with $SBR \leq 0.1$, cf. Fig. 4), useful isotopic
437 information about the sample can be extracted when sufficient large amount of weak
438 spectral features are present.

439 Simulation of U isotopic analysis by LIBS with U II 424.437 nm

440 The last simulation performed in this study is to compare the analytical performance of
441 LAMIS–LIBS combined approach in the 595 nm proximity to single emission-line
442 analysis with the U II 424.437 nm benchmark. This U II line was commonly used for
443 uranium isotopic analysis particularly with atomic emission [14, 46-50]. Simulation
444 shows that its averaged precision is 0.48% in absolute ^{235}U abundances, a notable value
445 for single-line analysis. The measured SBR for the strongest spectral features in the
446 LAMIS–LIBS spectrum (cf. Fig. 4) was only ~ 0.4 , whereas the SBR for the U II
447 424.437 nm line was substantially larger and was 1.38. As the flat component of plasma
448 background contains no extractable information but brings photon-shot noise, the
449 analytical performance of the LAMIS–LIBS combined analysis from a collection of
450 molecular bands and atomic lines is only similar to single-line analysis with the
451 benchmark U II line (cf. Fig. 5). Nevertheless, the LAMIS–LIBS combined approach
452 shows its potential as a viable supplement and valuable alternative for U isotopic analysis
453 in situation that the single U II 424.437 nm line suffers interference and cannot be
454 utilized. Because analyte signals (LIBS or LAMIS) are highly correlated, the use of
455 multiple spectral features as in the LAMIS–LIBS approach provides the necessary
456 resource for the PLS algorithm to differentiate the spectral patterns from the analyte
457 against those from spectral interferences [22] – an attribute that would be difficult to
458 implement if only a single spectral component (e.g., one atomic emission line) is used.

459 **Conclusions**

460 Isotopic analysis through the use of molecular spectrometry for the heaviest naturally
461 occurring element – uranium – was presented in this work. Spectral features and
462 characteristics of isotopic shifts for UO were identified. Through computer simulation,
463 the theoretical precisions attainable by LAMIS, LIBS and LAMIS–LIBS combined
464 approach for uranium isotopic analysis were studied. The analytical performance of
465 LAMIS with the most intense UO band at 593.4 nm (averaged simulated precision 1.5%)
466 was found to be slightly better than the use of a nearby single U I line (precision 1.6%)
467 with similar intensity but significantly smaller isotopic shift. The use of multiple (a total
468 of thirty-two) atomic emission lines improves the precision to 0.72%. Despite the fact
469 that many UO spectral characteristics appear weak (many with $SBR \leq 0.1$ due to intense
470 pseudo-continuum background), further inclusion of the molecular spectral features to the
471 multiple atomic lines (i.e., the LAMIS–LIBS combined approach) advances the precision
472 to 0.42%. Analytical performances of the LAMIS–LIBS combined approach compares
473 well with the U II 424.437 nm benchmark (precision 0.48%), and thus shows its potential
474 as a viable and valuable alternative for U isotopic analysis in situations that the
475 benchmark U II line cannot be used. The present study offers a better understanding on
476 the analytical performance of isotopic analysis with LAMIS and LIBS for uranium, in
477 which its spectral features (in particular its molecular spectroscopy) are complex,
478 generally unresolved and largely uncharacterized.

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623

624

625 **Table 1** Spectroscopic constants of the three U I lines used in the determination of
626 electronic excitation temperature of the LIBS plasma [45]

Wavelength (nm)	E_{lower} (cm ⁻¹)	E_{upper} (cm ⁻¹)	gA (s ⁻¹)
593.382	620	17468	2.8×10^6
594.277	5762	22584	5.8×10^6
594.857	7646	24452	1.2×10^7

627

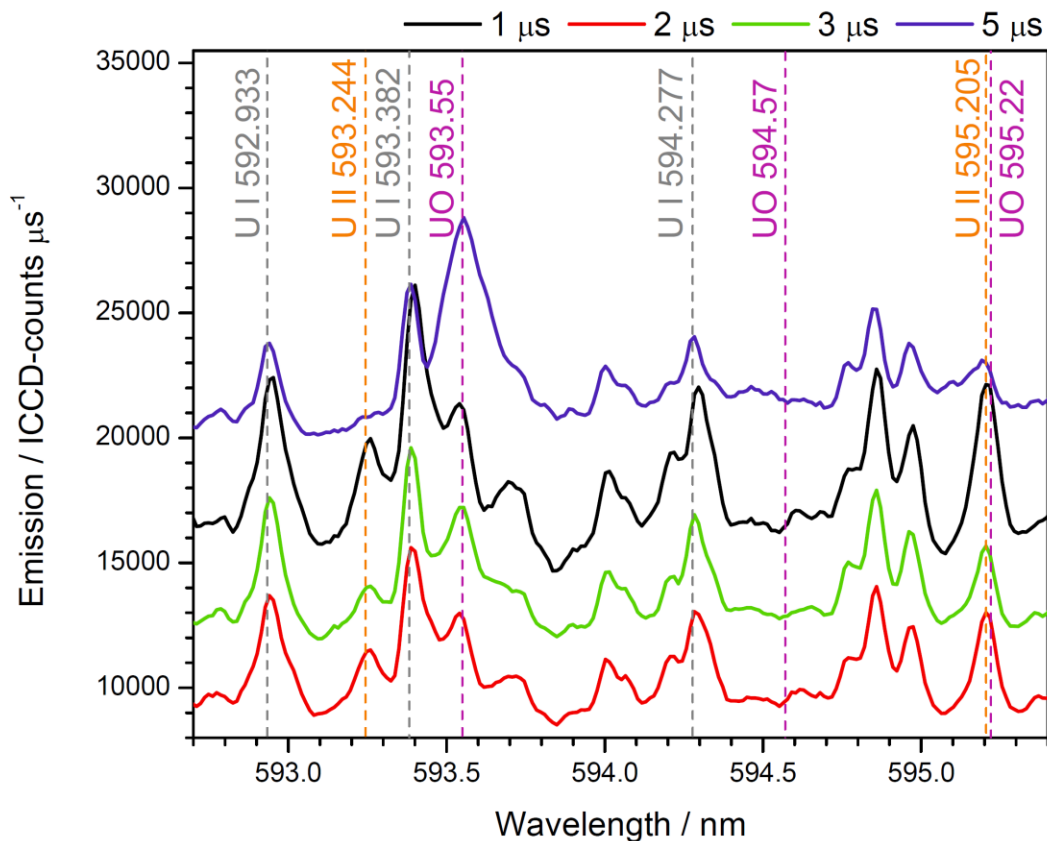
628 **Table 2** List of U I emission lines between 591.6 and 596.5 nm. Emission wavelengths
 629 for ^{238}U and their upper energy levels are taken from Palmer *et al.* [24] Isotopic
 630 shift (IS) data are calculated from the list published by Blaise and Radziemski
 631 [11]; a negative sign indicates that the ^{235}U wavelength is lower (i.e., blue
 632 shifted) than that of ^{238}U . Relative intensity is calculated based on the emission
 633 intensity given by Palmer *et al.* [24] for a hollow cathode discharge at 4400 K
 634 and rescaled to 5300 K through Boltzmann distribution.

^{238}U Wavelength (nm)	^{235}U - ^{238}U IS (pm)	E_{upper} (cm^{-1})	Relative intensity at 5300 K
591.9252	-9.63	28566	0.1118
591.9667	-10.16	23908	0.2338
592.2899	-10.52	27133	0.0585
592.3654	-23.86	28184	0.1960
592.3732	1.05	21329	0.1844
592.5316	-7.20	22634	0.1679
592.5455	7.20	24517	0.8746
592.9318	-17.93	20661	0.5754
592.9667	-12.48	24185	0.1245
592.9753	-12.48	27148	0.1225
593.3818	8.45	17468	1.0000
593.4844	Unknown*	29488	0.1162
593.5508	-10.57	23848	0.1408
593.7373	-8.11	27394	0.1462
593.9991	-9.17	24022	0.2414
594.0664	10.06	28285	0.1083
594.2769	-3.71	22584	0.5745
594.3412	25.08	23069	0.1760
594.7672	17.16	23057	0.3408
594.8170	-7.78	24940	0.0892
594.8566	-0.89	24451	0.7934

594.9662	-5.13	21078	0.3830
595.3650	-4.96	27477	0.0654
595.4372	-1.77	27475	0.1230
595.4673	4.96	26997	0.0597
595.4899	6.56	24906	0.2396
595.5620	-12.95	24650	0.0493
595.6812	-5.14	28341	0.0627
595.6859	-12.07	20651	0.8370
595.9944	-11.90	28451	0.1663
596.1901	-27.37	31270	0.0967
596.3940	-15.47	28053	0.1121

635 *isotopic shift for this line is unknown and is assumed to be zero (i.e., same wavelengths for ^{235}U
636 and ^{238}U) in the simulation.

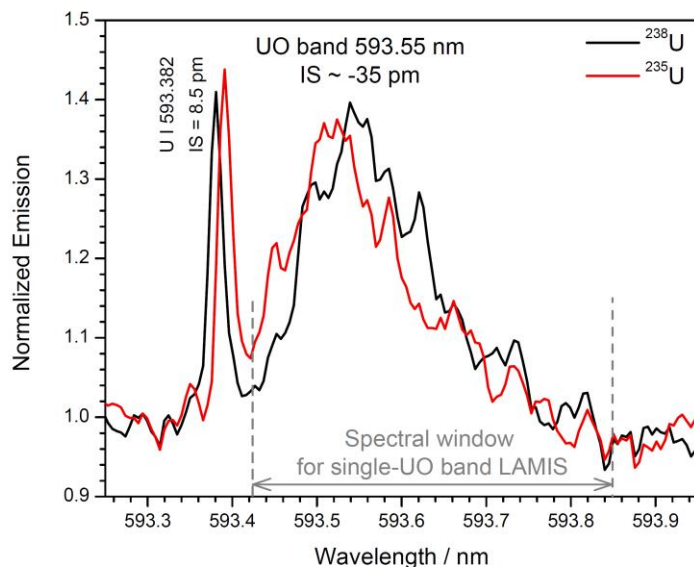
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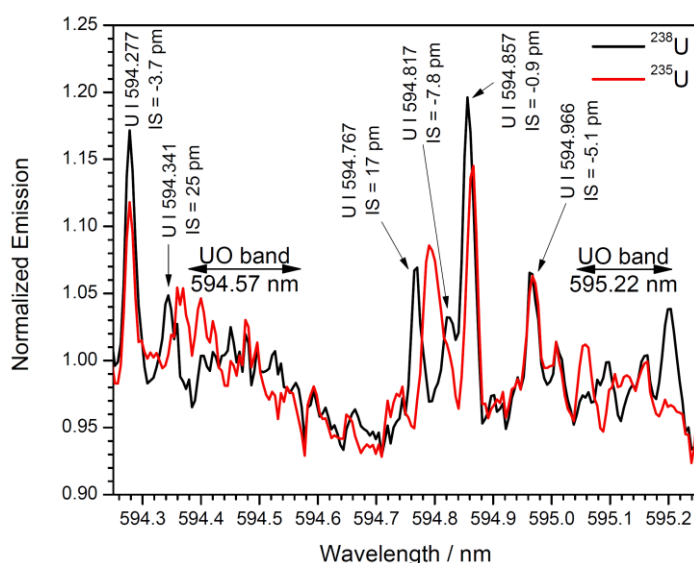
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639 **Fig. 1** Temporally resolved emission spectra at different ICCD delays from a depleted
 640 U_3O_8 pelletized sample. The ICCD gate widths were 1, 1, 2 and 4 μs ,
 641 respectively, for delays 1, 2, 3 and 5 μs . All emission is normalized to the gate
 642 width of the ICCD detector. A lower-resolution grating (1200 grooves/mm) was
 643 used for this spectral survey. The nominal wavelengths for atomic lines are
 644 referenced to ^{238}U

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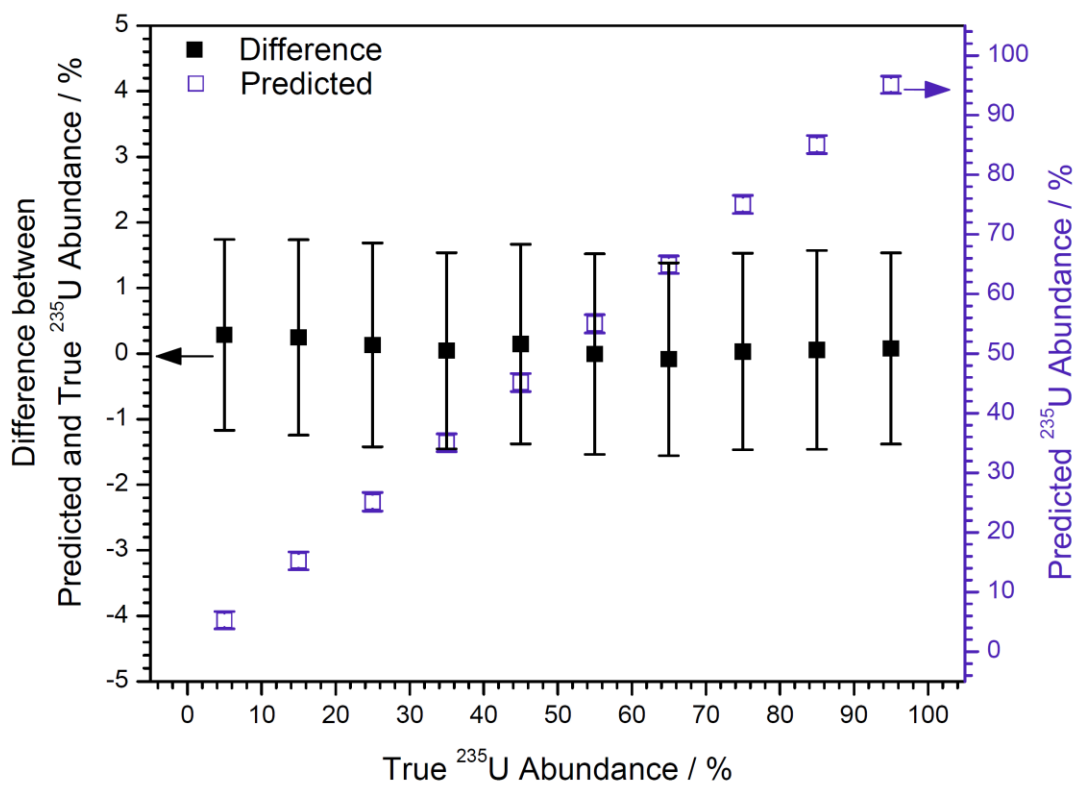


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648 **Fig. 2** ^{235}U and ^{238}U base spectral profiles of some selected atomic lines and molecular
 649 bands exhibiting distinct isotopic shifts. (a, top) The intense UO band at 593.55
 650 nm and its neighboring UI line at 593.382 nm (with their isotopic shifts). The
 651 marked region shows the base profiles used in the single UO-band LAMIS
 652 simulation. (b, bottom) A 1-nm window from 594.25 to 595.25 nm showing
 653 different emission patterns, in addition to isotopic shifts, of two UO bands. All
 654 spectra were recorded with a 2400 grooves/mm grating. The nominal
 655 wavelengths for atomic lines are referenced to ^{238}U

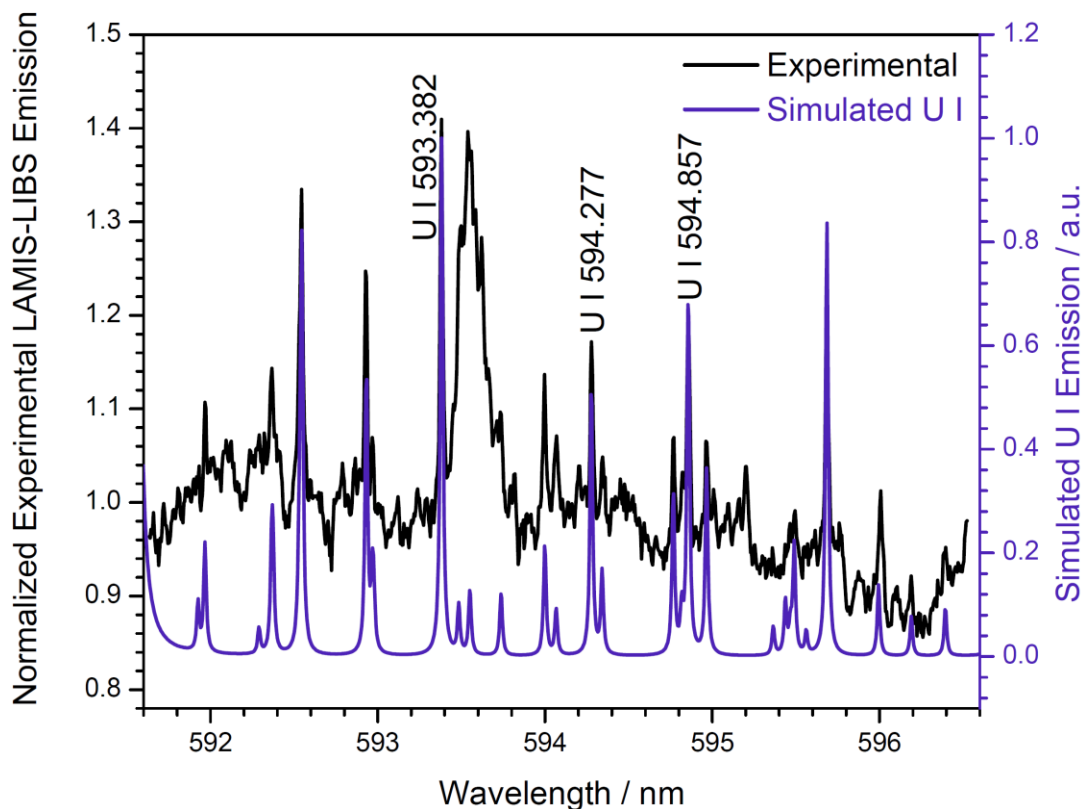


656

657 **Fig. 3** Analytical bias and precision (left axis) and determined isotopic abundances of
 658 ^{235}U (right axis) against known ^{235}U abundances in the simulation. The
 659 calibration set contained eleven standards with equally spaced ^{235}U abundances
 660 from 0% to 100%. All simulated spectra (both the samples and the calibration
 661 standards) were accumulated from 10 laser shots

662

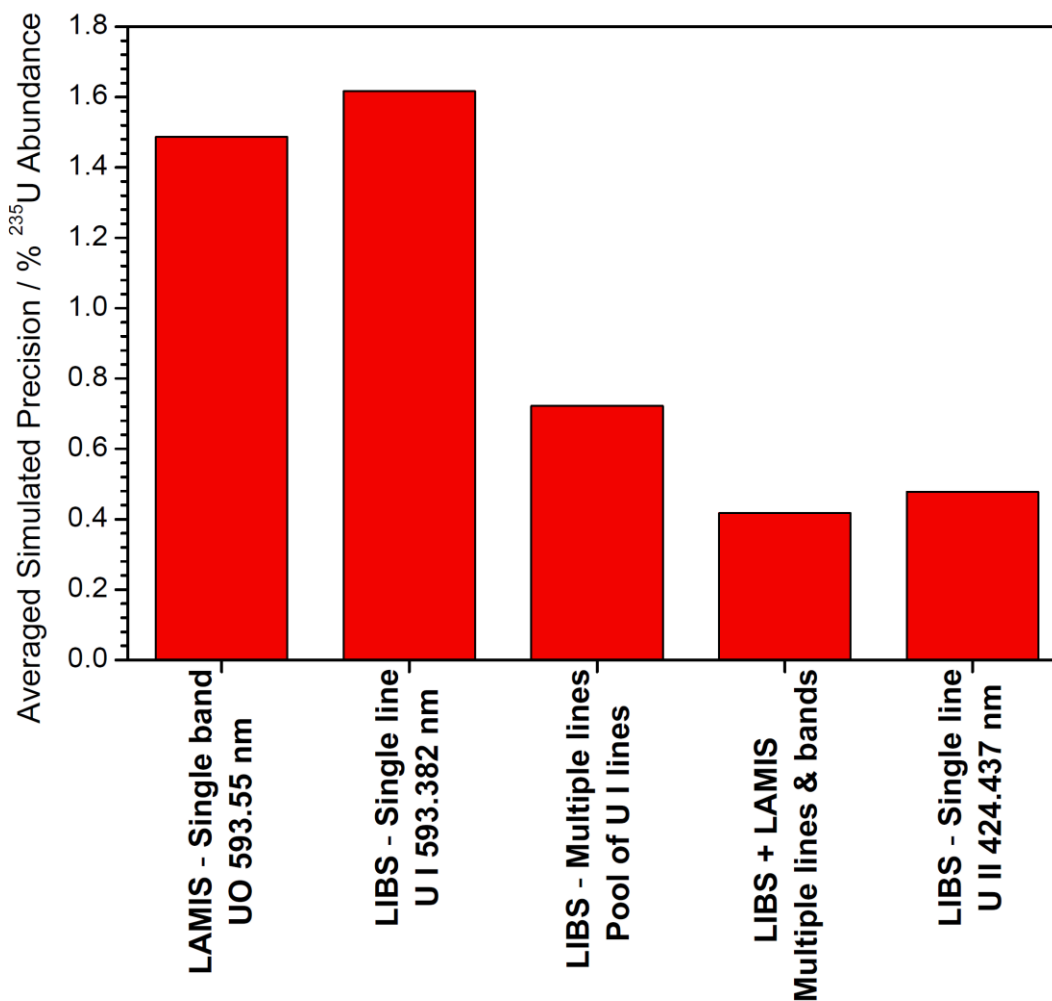
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664

665 **Fig. 4** Experimentally measured ^{238}U LAMIS-LIBS (molecular bands together with
 666 atomic lines) spectrum, and the simulated U I lines with an electronic excitation
 667 temperature of 5300 K. The three labelled U I lines are those employed in the
 668 Boltzmann plot for the evaluation of excitation temperature. The experimental
 669 spectrum was recorded with a depleted U_3O_8 sample and a 2400 grooves/mm
 670 grating

671



672

673 **Fig. 5** Averaged simulated precision (in percentage ^{235}U abundance) when different
674 atomic and molecular spectral features are incorporated into the PLS calibration
675 model

676