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CELL DESIGN FOR LASER-INDUCED BREAKDOWN
SPECTROSCOPY MEASUREMENTS
ON REACTIVE GAS SAMPLES

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KEYWORDS: Uranium hexafluoride; Laser-Induced Breakdown Spectroscopy, Reactive gas

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24 **Abstract**

25 Uranium hexafluoride (UF_6) is the primary material used for the enrichment of uranium in the
26 production of light water nuclear reactor fuels worldwide. Accurate, rapid quantification of uranium
27 isotopic composition in nuclear materials is required for safeguards programs and nonproliferation
28 purposes. One potential technique for isotopic measurements in uranium species in the field is laser
29 induced breakdown spectroscopy (LIBS). Safe and effective application of LIBS to UF_6 for enrichment
30 measurements is uniquely challenging due to the chemical and physical properties of UF_6 , which
31 necessitate specific handling procedures. The objective of this work is to design a cell for isotopic
32 analysis of UF_6 that is (1) compatible with chemical and physical properties of UF_6 , (2) compatible with
33 LIBS laser, and (3) portable-sized for nuclear safeguards applications. Along with cell design, initial
34 testing of the cell for basic performance and chemical compatibility is performed. As designed and
35 constructed, the portable gas cell was gas-tight, chemically compatible with UF_6 , and withstood long-
36 duration laser exposure. The cell has proven capability for handling reactive gases, such as UF_6 , with
37 specification application to isotopic analysis.

38

39 **1. Introduction**

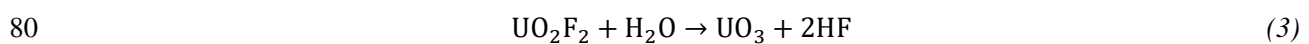
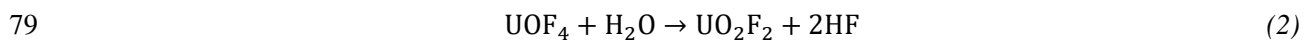
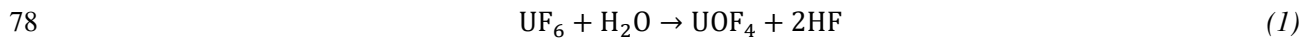
40 Nuclear safeguards programs seek to verify declared uranium enrichment at nuclear facilities
41 worldwide for nonproliferation purposes, requiring accurate and rapid quantification of uranium isotopic
42 composition in nuclear materials. Uranium hexafluoride gas ($\text{UF}_{6(g)}$) is used for isotopic separation and
43 enrichment of uranium by gaseous diffusion or centrifugation [1], making it a key compound in the
44 nuclear fuel cycle and critical for safeguards measurements. Non-destructive analysis (NDA) is a
45 prevalent method for monitoring the enrichment of uranium because it can be performed in field settings
46 without having to send samples to a laboratory [2]. The most commonly used NDA technique for
47 monitoring uranium enrichment is gamma spectroscopy [2]. The advent of field-portable and handheld
48 gamma spectrometers has led to rapid onsite enrichment verification for safeguards applications.

49 However, gamma spectrometers can have limitations on precision of measurements. Destructive analysis
50 techniques, such as mass spectrometry, can achieve precise isotopic measurements for uranium
51 enrichment verification and are the most sensitive analytical method available. Techniques such as
52 thermal ionization mass spectrometry (TIMS) and multi-collector inductively coupled plasma mass
53 spectrometry (MC-ICP-MS) are used to analyze uranium isotopic composition for safeguards applications
54 [2]. Mass spectrometry techniques are extremely sensitive, but they are also costly and time consuming,
55 and samples must be sent off site to a certified laboratory for processing and analysis. New shipping
56 regulations make it difficult to transport UF₆.

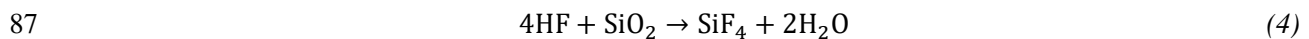
57 Laser induced breakdown spectroscopy (LIBS) is a potential technique for field-portable
58 measurement of isotopic composition, with noteworthy application in nuclear safeguards work. LIBS is
59 an atomic optical emission spectroscopic technique that utilizes pulsed lasers to generate a plasma and
60 vaporize the sample; optical emissions are recorded by spectrometer [3]. LIBS can be used for both
61 elemental and isotopic analysis. Because LIBS does not require sample preparation, it is potentially an
62 excellent option for field measurements of elemental and isotopic composition. Over the last two decades,
63 the technology has been developed to make portable LIBS systems for accurate field measurement of
64 isotopic composition [4-6], advancing the applications of this technique beyond the laboratory setting and
65 making it attractive for safeguards work. Methods for isotopic measurements of uranium in nuclear
66 materials [7-9] and uranium in soil [10] have been established for LIBS, but these methods only focus on
67 measurements in the solid state. An approach for measurement of the isotopic composition of UF₆ in its
68 gaseous state was recently developed [11], expanding the relevance of LIBS beyond the solid state for
69 uranium isotopic measurements. Previous studies by Chan *et al.* [11] provide detailed analytical
70 characterization of the LIBS system for gaseous uranium, including isotopic analysis, detector settings,
71 and laser parameters.

72 Specialized handling techniques and materials of construction are required to safely handle UF₆,
73 adding a unique challenge to the application of LIBS for UF₆ enrichment measurements. UF₆ is a white

74 crystalline solid at room temperature, but with a significant vapor pressure at room temperature [1, 12]
75 and with the triple point occurring at 64.02°C and 1137.72 Torr [13]. While UF₆ does not readily react
76 with dry air, in the presence of water vapor [14], UF₆ will hydrolyze [15-19] to generate hydrogen
77 fluoride (HF) and UO₂F₂ according to the series of reactions presented below [18]:



81 The reactions presented in Eqs. (1) and (2) occur very rapidly at normal atmospheric conditions, and the
82 reaction given in Eq. (3) occurs very slowly, except at high temperatures. The HF formed in these
83 hydrolysis reactions may be in the form of HF(g), or it may be an HF fog consisting of miniscule droplets
84 of HF–water solution: the form it takes is dependent on humidity and temperature [14]. HF is acutely
85 toxic [20] and presents significant human health risks if released. Another consequence of UF₆ hydrolysis
86 and HF formation is the subsequent reaction of HF with glass and fused silica [15]:



88 This reaction generates a new supply of water, which can, in turn, feed the reactions presented in Eqs. 1–
89 3, resulting in a constant cycle of HF generation. Over time, this reaction etches the glass and can
90 eventually cause breakdown of glass vessels, leading to potential release of stored UF₆. To prevent these
91 types of reactions, UF₆ samples must be kept under vacuum conditions in completely sealed systems [13,
92 14, 20], and careful precautions must be taken in handling UF₆ samples to (1) prevent any moisture from
93 entering the system and (2) to prevent leaks of UF₆ samples into the atmosphere. UF₆ samples can be
94 stored in glass, although it is recommended that vessels be degassed and flamed prior to use [15].
95 Moreover, a thoroughly dried potassium or sodium fluoride salt “getter” [1, 15] should be included to
96 prevent HF buildup. UF₆ is also chemically compatible with fluorinated materials such as Teflon [1].
97 Besides its potential reactivity with water and glass, UF₆ is a strong fluorinating compound, and as such,

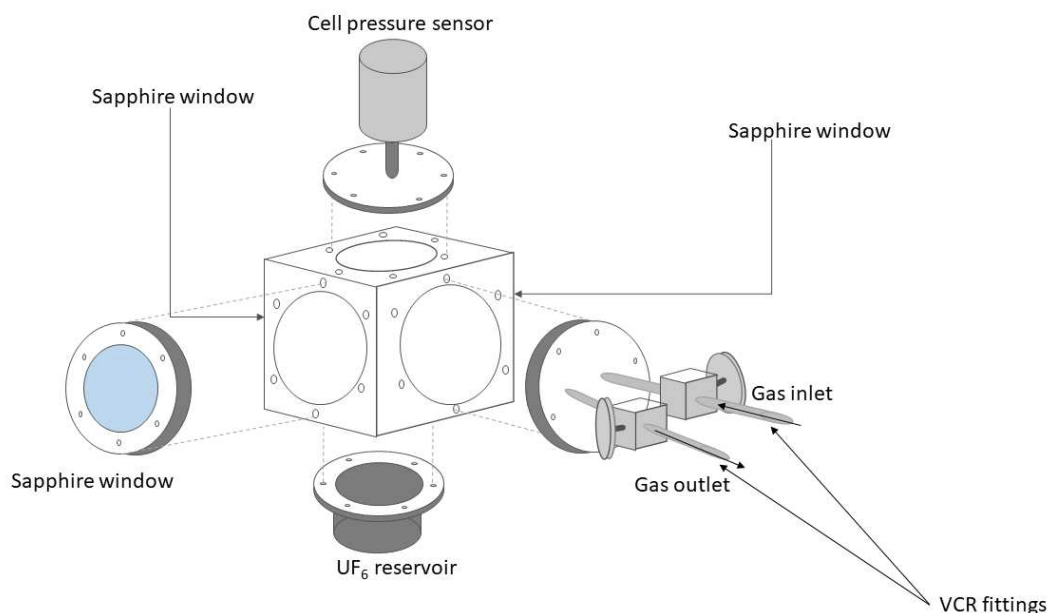
98 it can attack metals [1, 14, 16]. Therefore, it is recommended that UF₆ be handled in stainless steel or
99 other metals alloyed with nickel [1, 16].

100 Best practices for UF₆ handling in a laboratory or industrial setting are well documented in the
101 literature [13, 14, 20]. However, no design or practices for a UF₆ handling and measurement system with
102 specific applicability to LIBS have been reported. The cell under development in this effort must (1) meet
103 the various chemical and physical challenges posed by UF₆ handling related to reactive gas chemistry, (2)
104 be compatible with the low-energy laser and resultant plasma, and (3) retain a portable size to be relevant
105 for the desired uranium enrichment monitoring needed for nuclear safeguards applications. The objectives
106 of the present work are (1) to design a cell for isotopic analysis of UF₆ using LIBS and (2) to test the cell
107 for basic performance, chemical compatibility, and potential sample carryover between measurements.
108 For this work, the emphasis is on portability of the gas cell, not the entire measurement setup. Besides
109 UF₆ measurements, the cell conceived in this study, along with the associated handling techniques, have
110 potential applicability to other reactive gases such as fluorine and chlorine compounds, which have
111 physical and chemical properties, as well as handling challenges, that are similar to UF₆.

112

113 **2. Results & Discussion**

114 The finalized design for a self-contained LIBS cell for use with UF₆ is shown in Figure 1, with
115 full details of cell design and components described in Experimental section. The cell consists of a
116 Kimball Physics spherical cube vacuum chamber 6.985 cm wide with 3 sapphire viewports (2.0 mm
117 thickness) mounted into a 6.985 cm conflat flange (MDC Precision), a custom-designed flange with gas
118 inlet/outlet valves (Swagelok), a pressure transducer (902B MKS instruments), and a custom-designed
119 reservoir for excess solid UF₆ (Accu-Glass Products, Inc.). All conflat flanges were sealed to the spherical
120 cube using copper gaskets.



121

122 **Figure 1.** CAD drawing of the final cell design with three sapphire windows.

123

124 During initial testing in a cube-like chamber at the Lawrence Berkeley National Laboratory
 125 (LBNL), a laser-induced plasma was generated in 50–100 Torr air with a gaseous surrogate analyte,
 126 (methylcyclopentadienyl) manganese tricarbonyl (MMT), at <0.1 Torr. The optical emission from the
 127 plasma was collected at 90° from the laser with a focusing lens. Figure 2a depicts the measured emission
 128 from the Mn present in MMT at 257.610, 259.372, and 260.568 nm. However, during this experiment,
 129 several other atomic emission lines grew in that did not belong to Mn, especially when a higher laser
 130 pulse energy was used. Figure 2b depicts an example emission spectrum recorded when the laser pulse
 131 energy was increased to 134 mJ. These additional peaks were identified as being associated with Fe and
 132 Cr. Upon examination of the cell (Figure 3), it became apparent that the Fe and Cr peaks originated from
 133 the stainless-steel backstop of the surrogate cell. This finding resulted in the third sapphire window being
 134 installed in the cell that was to be used for UF₆ so that the laser light could exit the cell without damaging
 135 it and a backstop installed outside of the chamber.

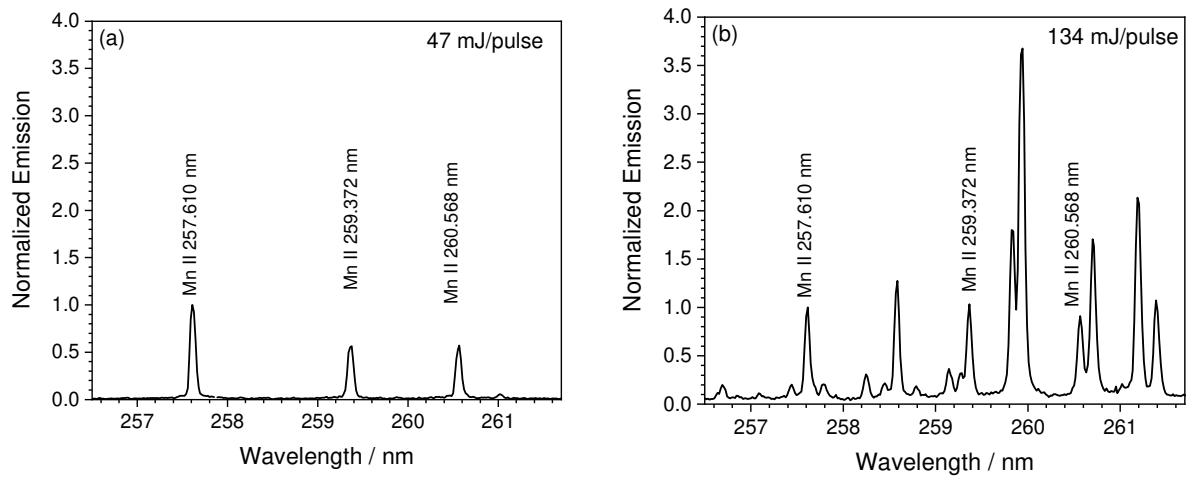


Figure 2. Measured LIBS emission spectra with low-pressure gaseous surrogate (methylcyclopentadienyl) manganese tricarbonyl (MMT) under laser pulse energies of (a) 47 mJ and (b) 134 mJ.



Figure 3. Laser ablation mark on the surrogate cell backstop plate.

137 Cell leak tests using pressure measurements indicated a leak-tight system. The measured pressure
 138 change was acceptable (Table 1), indicating that the cell was gas tight, preventing UF₆(g) escaping the
 139 cell or in-leakage of air. The diminishing rate of increase in the pressure change is only indicative of
 140 outgassing from the inner surface of the cell rather than in-leakage. As a precaution, a long-term
 141 experiment was initiated in which the cell was filled with 69.96 Torr UF₆, sealed, and left for a long-term
 142 exposure test. The pressure of this cell was monitored with the MKS pressure transducer for 100 days,
 143 and no statistically significant pressure changes were observed during this time. This result is consistent
 144 with the measurements presented in Table 1.

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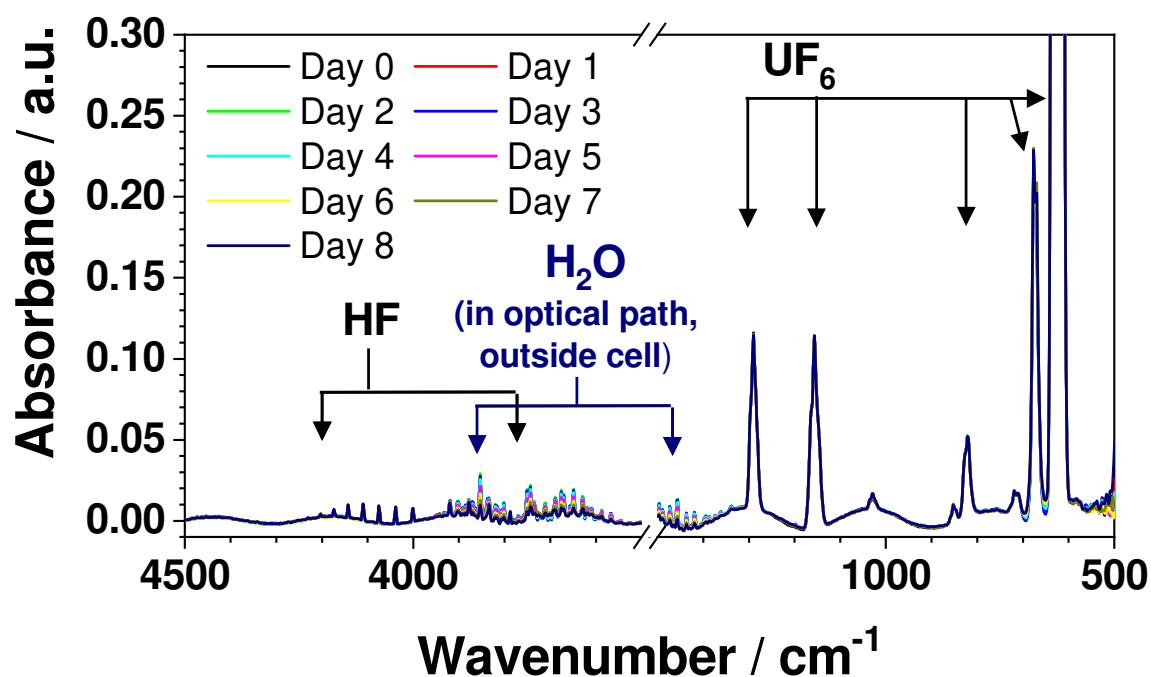
146 **Table 1.** Pressure over time for 3 cell leak tests.

Test 1		Test 2		Test 3	
Time (days)	Pressure (Torr)	Time (days)	Pressure (Torr)	Time (days)	Pressure (Torr)
0	4.70E-04	0	7.10E-05	0	4.20E-05
1	9.60E-04	1	1.40E-04	2	1.00E-04
2	1.10E-03	2	1.80E-04	3	1.20E-04
3	1.30E-03	3	2.00E-04	4	1.30E-04
4	1.40E-03	4	2.20E-04	5	1.40E-04
5	1.60E-03	5	2.40E-04	6	1.60E-04

147

148 The cell material's compatibility with the laser system was determined through extended laser
 149 testing on a cell made at the Oak Ridge National Laboratory (ORNL) that was filled with 60 Torr N₂ and
 150 shipped to LBNL for testing. When the cell was returned to ORNL, there was no observable optical
 151 damage to the sapphire windows, indicating that the sapphire withstood the repetitive laser firings at full
 152 pulse energy (~130 mJ). After the visual inspection, the cell was connected to a manifold, and UF₆ was
 153 circulated through it. Fourier-transform infrared (FTIR) measurements of the cell after UF₆ addition
 154 showed no reaction with UF₆. Based on these results, it was concluded that firing the laser through the
 155 cell had no detrimental effect to the inner surfaces that would make them reactive towards UF₆.

156 To further probe the chemical compatibility of the cell's interior components and verify that the
157 cell was leak-tight, a cell was constructed with ZnSe windows so that it could undergo FTIR analysis for
158 an extended period of time. Figure 4, which depicts the FTIR spectra recorded over 8 days of
159 measurements, shows little change in the intensity of the UF_6 peaks, and only small peaks consistent with
160 HF. If there had been a leak in the cell, the UF_6 would have reacted with water to produce an increasing
161 quantity of HF. The lack of ingrowth of HF over the 8-day period indicates that there was no significant
162 leakage or permeation of water or water vapor into the cell. Overall, the FTIR data indicate that $\text{UF}_6(\text{g})$
163 was chemically stable in the cell as designed and corroborate the conclusion from the pressure
164 measurements that the cell is leak-tight.
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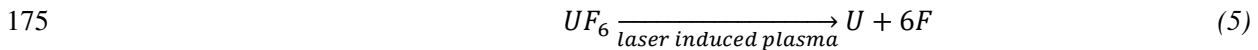
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167 **Figure 4.** Time-resolved Fourier-transform infrared (FTIR) spectra of $\text{UF}_6(\text{g})$ sample in cell.

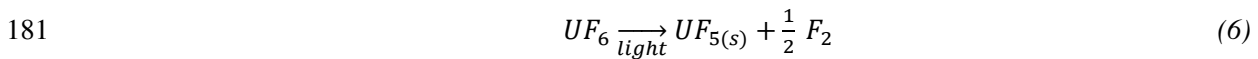
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169 After the compatibility testing, a cell containing 1.13 g of natural enrichment UF_6 (0.711 wt-%)
170 was sent to LBNL for testing. This allowed for a saturated vapor of UF_6 to be present in gaseous form

171 inside the cell, along with solid UF₆ in the reservoir at the bottom of the cell (Figure 5). The reserve
172 amount of solid UF₆ was added to the cell because it was assumed that the generation of the plasma inside
173 the cell would destroy the UF₆ molecule entirely to its constituent atoms through an atomization reaction
174 such as depicted in Equation (5).



176 Therefore, additional solid UF₆ in the reservoir could be used to replenish the saturated vapor phase if
177 UF₆ were destroyed by the reaction in Equation (5). Another concern for the destruction of UF₆
178 molecules in the vapor phase is photo-dissociation reactions. The photo-dissociation of gaseous UF₆ to
179 solid UF₅ is shown in Equation 6 and is feasible with the laser light, or with the emission from the laser-
180 induced plasma, as discussed in previous work [11]:



182 To arrest and partially reverse the forward photo-dissociation reaction shown in Equation (6), 20 Torr of
183 F₂ was also added to the cell prior to shipping. Because the volume of the plasma could not be accurately
184 measured, approximate values were utilized to calculate a conservative number of laser shots—60,000
185 [11]—that would result in the consumption of all the UF₆.

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188

189 **Figure 5.** Excess UF_6 solid in the reservoir of the cell.

190 The initial experiments performed with this mixture of UF_6 and F_2 in the headspace of the cell did
191 not lead to any visible deposition of solid materials on the interior surfaces of the cell. In addition, no
192 significant change of pressure was noted beyond what could be explained by day-to-day fluctuations of
193 room temperature. According to the reaction shown in Eq. (6), if UF_6 is photo-dissociated to UF_5 , then a
194 change of pressure could be expected, along with precipitation of solid UF_5 . This suggests that most of
195 the uranium and fluorine atoms in the plasma recombined to form UF_6 molecules. As such, additional
196 samples that were sent to LBNL for testing only contained UF_6 of the desired assay. The second and third
197 cells sent for long-term analysis contained natural and 4.62 wt-% enriched UF_6 from ORNL stocks.
198 During the course of testing with these samples, it was determined that there was no notable degradation
199 of UF_6 caused by firing the laser and subsequent plasma generation into the chamber. This suggests that,
200 moving forward, it would not be necessary for the samples to have a reserve in the bottom of the cell. The
201 cell could simply contain UF_6 in the headspace at approximately 70 Torr.

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205 **3. Conclusions**

206 A cell was designed for isotopic analysis of UF₆ using LIBS. The cell design required careful
207 attention to and testing of the chemical compatibility of UF₆ with materials of construction, as well as
208 compatibility of materials with the laser and the LIBS plasma. Testing of the cell revealed a gas-tight
209 system, excellent chemical compatibility of parts with UF₆, as well as good performance of sapphire
210 windows under long-duration laser exposure. As constructed and tested, the cell has proven capability for
211 handling and subsequent isotopic analysis of reactive gases such as the UF₆ used in this study. This
212 capability can likely be extended to testing of other fluorine and chlorine compounds with comparable
213 chemical handling complications, thus opening the door for enhanced isotopic analysis of challenging
214 reactive gas systems using LIBS techniques.

215

216 **4. Experimental**

217 Caution! UF₆ is radioactive and forms highly toxic hydrogen fluoride in the presence of water. Safe
218 handling requires appropriate facilities and qualified personnel. All handling and testing were performed
219 in sealed manifolds and/or cells.

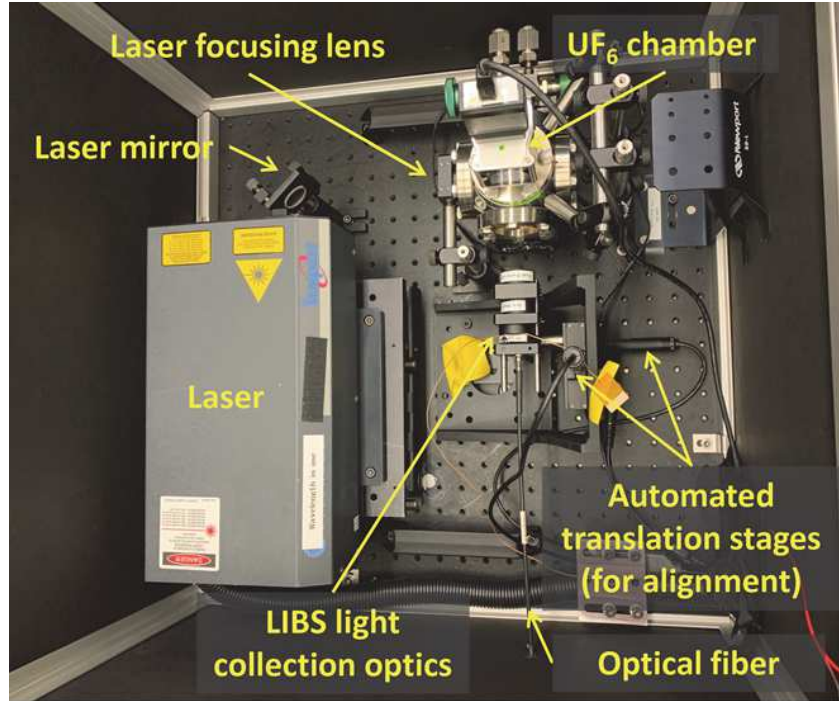
220 *4.1 Cell Design*

221 The initial cell design was adapted from one used to study low pressure LIBS of (methyl
222 cyclopentadienyl) manganese tricarbonyl (MMT) at LBNL. The preliminary design for a self-contained
223 cell for use with UF₆ is shown in Figure 1. The initial cell consisted of a spherical cube (Kimball Physics)
224 6.895 cm. wide with 2 sapphire windows at right angles to each other. However, as a result of issues
225 identified during testing with the MMT at LBNL, a third sapphire window was added in place of a blank
226 stainless-steel plate opposite the laser entry window. The laser light that was used to form the plasma
227 entered and exited through the two sapphire windows that were opposite to each other, and the sapphire
228 window that was perpendicular to these windows was used to collect the light emitted from the plasma.

229 The remaining three faces of the spherical cube consisted of a custom-designed flange with gas
230 inlet/outlet valves, a pressure transducer (MKS 902B), and a custom-designed reservoir (Accu-Glass
231 Products, Inc.) for excess solid UF₆.

232 Sapphire was chosen as the material of construction for the windows because of its excellent
233 corrosion resistance to UF₆ [21] and its large optical transmission window (0.15 --4.5 μm) [22] for
234 analytical measurements. The primary reason for the choice of the MKS 902B pressure transducer for use
235 in the cell was the chemical resistivity of the wetted surfaces to UF₆. Prior to any testing, the inner cell
236 surfaces were dried and then passivated. The passivation process included holding the cell under vacuum,
237 filling it with dry N₂ gas, evacuating the cell, and finally, filling the cell with F₂ gas (>99% purity) and
238 exposing for 72 hrs. The cell was subsequently evacuated for use and testing with UF₆.

239 To develop of a smaller, self-contained system, a light-proof enclosure was designed to house the
240 LIBS system and the UF₆ cell. The container not only served to decrease the footprint of the system, but it
241 also enclosed the Class 4 laser (Nd:YAG laser, wavelength 1064 nm) that was used for the LIBS
242 measurements. With a well-engineered interlock system, the operator outside the enclosure has no
243 exposure to the laser, the whole system, by definition, is a Class-1 laser product, which is laser safe for
244 the operator. Class-1 laser products are the lowest hazard class, thus making the system safer and easier to
245 operate. The laser, a laser beam-directing mirror, the UF₆ cell, the beam stop, and the optical lenses and
246 fibers (Figure 6) are all contained inside the enclosure. Also, a Peltier cooler was situated beneath the UF₆
247 cell to maintain the UF₆ at a constant partial pressure of 15 Torr during measurements.



248

249 **Figure 6.** Photograph of interior of enclosure for laser (left) and UF₆ cell (top right).

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254 *4.2 Cell Testing*

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To leak test the cell, it was attached to a low-volume vacuum manifold, where it was evacuated and filled with dry N₂ three times to remove water from the interior surfaces. This pressure cycling also served as an internal check for the pressure sensor mounted directly to the cell. Cell volumes were determined by performing gas expansion tests through various sections of known volumes in the vacuum manifold and by applying the following:

260

$$\frac{P_1 V_1}{P_2} = V_2 \quad (7)$$

261

262

Where P is pressure and V is volume of the cell. Average cell volumes were found to be approximately 270 cm³. The cells were evacuated to below 10⁻⁵ Torr on a custom manifold fabricated at ORNL

263 (measured from the test loop equipment *Granville-Phillips ion gauge*), isolated, and removed from the
264 loop. As a result of minor differences in manufacturing processes, the volume for each cell must be
265 determined individually; the approximate cell volume of the final cell was determined to be $\sim 272.48 \text{ cm}^3$.

266 Over the course of 7 days, the pressure was monitored on the sensor attached to the cell, and no
267 increase was observed. Following these tests, the interior of the cells was fluorinated to passivate the
268 interior surfaces. The cells were filled with F_2 and evacuated three times to pressures of 10.2 Torr, 30.2
269 Torr and 100.3 Torr. After the final evacuation, both cells were filled with dry N_2 . After this treatment, a
270 cell was filled with 99.4 Torr dry N_2 (at 296.76 K / 23.61 °C) and was shipped to LBNL for testing with
271 repetitive laser firings under the maximum pulse energy ($\sim 130 \text{ mJ}$) of the laser. It should be noted that
272 the typical laser pulse energy for UF_6 enrichment assay is much less than this maximum energy and
273 should be 40 mJ or less [11]. Extended laser testing with maximum pulse energy was performed to
274 determine the materials' compatibility with laser pulses. The extended laser testing lasted for a total of
275 130 hours (i.e., $130 \text{ hr} \times 3,600 \text{ s/hr} \times 10 \text{ laser pulses/s} = 4.7 \text{ million laser pulses}$), and no damage on the
276 window was found.

277 After the repetitive laser-firing test, the cell was shipped back to ORNL for UF_6 compatibility
278 testing. On receipt of this cell at ORNL, it was attached to a manifold and evacuated. The UF_6 manifold
279 was set up in a configuration that circulated UF_6 through the cell and through a gas cell attached to an
280 ABB MB3000 FTIR spectrophotometer. The manifold was filled with $\sim 30 \text{ Torr UF}_6$, and this was
281 circulated through the system for several days. Infrared spectra (4 cm^{-1} resolution, 8 scans from 500 to
282 $5,000 \text{ cm}^{-1}$) were recorded periodically during the 5-day run to measure for UF_6 and for the presence of
283 HF or other degradation products. This experiment was repeated twice.

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292

293 **Author Contributions**

294 The manuscript was written through contributions of all authors. All authors have given approval to the
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296

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Graphical Abstract

