The Pennsylvania State University
The Graduate School

HYBRID INTERFEROMETRIC/DISPERSIVE ATOMIC SPECTROSCOPY FOR NUCLEAR MATERIALS ANALYSIS

A Dissertation in
Nuclear Engineering
by
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Abstract

Laser-induced breakdown spectroscopy (LIBS) is an optical emission spectroscopy technique that holds promise for detection and rapid analysis of elements relevant for nuclear safeguards and nonproliferation, including the measurement of isotope ratios. One important application of LIBS is the measurement of uranium enrichment ($^{235}\text{U}/^{238}\text{U}$), which requires high spectral resolution (e.g., 25 pm for the 424.437 nm U II line). Measuring uranium enrichment is important in nuclear nonproliferation and safeguards because the uranium highly enriched in the $^{235}\text{U}$ isotope can be used to construct nuclear weapons. High-resolution dispersive spectrometers necessary for such measurements are typically bulky and expensive. A hybrid interferometric/dispersive spectrometer prototype, which consists of an inexpensive, compact Fabry-Perot etalon integrated with a low to moderate resolution Czerny-Turner spectrometer, was assembled for making high-resolution measurements of nuclear materials in a laboratory setting. To more fully take advantage of this low-cost, compact hybrid spectrometer, a mathematical reconstruction technique was developed to accurately reconstruct relative line strengths from complex spectral patterns with high resolution. Measurement of the mercury 313.1555/313.1844 nm doublet from a mercury-argon lamp yielded a spectral line intensity ratio of 0.682, which agrees well with an independent measurement by an echelle spectrometer and previously reported values.

The hybrid instrument was used in LIBS measurements and achieved the resolution needed for isotopic selectivity of LIBS of uranium in ambient air. The samples used were a natural uranium foil (0.7% of $^{235}\text{U}$) and a uranium foil highly enriched in $^{235}\text{U}$ to 93%. Both samples were provided by the Penn State University’s Breazeale Nuclear Reactor. The enrichment of the uranium foils was verified using a high-purity germanium detector and dedicated software for multi-group spectral analysis. Uranium spectral line widths of $\sim$10 pm were measured at a
center wavelength 424.437 nm, clearly discriminating the natural from the highly enriched uranium at that wavelength. The 424.167 nm isotope shift (~6 pm), limited by spectral broadening, was only partially resolved but still discernible. This instrument and reconstruction method could enable the design of significantly smaller, portable high-resolution instruments with isotopic specificity, benefiting nuclear safeguards, treaty verification, nuclear forensics, and a variety of other spectroscopic applications.
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**List of Acronyms and Initialisms**

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<td>LIBS</td>
<td>laser-induced breakdown spectroscopy</td>
<td>1</td>
</tr>
<tr>
<td>IAEA</td>
<td>International Atomic Energy Agency</td>
<td>1</td>
</tr>
<tr>
<td>NPT</td>
<td>Nuclear Non-Proliferation Treaty</td>
<td>2</td>
</tr>
<tr>
<td>NDA</td>
<td>non-destructive analysis</td>
<td>3</td>
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<tr>
<td>TIMS</td>
<td>thermal ionization mass spectrometry</td>
<td>5</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>inductively coupled mass spectrometry</td>
<td>5</td>
</tr>
<tr>
<td>ICCD</td>
<td>intensified charge-coupled device</td>
<td>9</td>
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<td>LAMIS</td>
<td>laser ablation molecular isotopic spectrometry</td>
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<tr>
<td>LTE</td>
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<td>FWHM</td>
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<td>FSR</td>
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Dedication

To B.W.M.
Chapter 1

Introduction

The technical needs of the non-proliferation community provide the context for current research directions in nuclear detection and equipment development. The legal entities that help ensure safeguards benefit from having a broad and diverse set of tools and technologies to meet their objectives for mitigating the development and spread of nuclear weapons around the world. This chapter begins with a brief history of the political and technical forces that drive present-day research and development of novel technologies for detection of nuclear material. What follows is an overview of the equipment and techniques that are currently used for nuclear safeguards monitoring inspections. New technologies such as laser-induced breakdown spectroscopy (LIBS) are currently being tested and evaluated for routine use in inspections.

1.1 Nuclear nonproliferation and safeguards

Since the beginning of the nuclear age, the international community has been challenged with the dual role of managing the development of peaceful nuclear technology while preventing nuclear proliferation. The International Atomic Energy Agency (IAEA) was created in 1957 as a result of Atoms for Peace program as
a legal entity with the authority to verify that states were not illicitly producing or spreading nuclear weapons while developing nuclear technology for peaceful purposes, exclusively. In 1970 the Treaty on the Non-Proliferation of Weapons (NPT) entered into force, forming a safeguards system that expanded and strengthened the role of the IAEA. The IAEA enters into agreements with NPT states to verify that a state is not developing, acquiring or distributing nuclear weapons or technologies. In addition to providing the legal framework for safeguards, nonproliferation incorporates regional security agreements, export control treaties, national policies, and other forms of nuclear cooperation [1, 2].

The implementation of nuclear safeguards continues to evolve and has expanded beyond routine inspections to include measures including unannounced inspections, approaches designed to account for concealment, and consideration of different diversion pathways. Inspection tools such as environmental sampling, which the IAEA began conducting in the 1990s, have been developed as an effective supplement to detecting undeclared proliferation activities. Because the task of verifying compliance requires the ability to measure the quantities of nuclear material\(^1\) present in a facility, the evolution of safeguards has been accompanied by advanced technologies and equipment for verification methods for material accounting, surveillance, and environmental sampling [4]. Technology for nuclear safeguards continues to evolve as research and development improves monitoring and sensing of nuclear materials. Technological developments have been driven by the need to improve the effectiveness of monitoring to include remote sensing capability, greater instrument sensitivity and selectivity, speed and portability [5].

\(^{1}\)The IAEA definition of *nuclear material* is used in this dissertation, and refers to isotopes (e.g., of uranium, plutonium, thorium) that can be used to make nuclear weapons [3].
1.1.1 Technical objectives

The most critical stage in nuclear weapons development is obtaining a sufficient quantity of fissile material. Safeguards focus on the elemental and isotopic analysis of uranium and plutonium. One of the primary aims of safeguards is to ensure that nuclear material inventories match the amounts declared by nuclear facilities. Furthermore, safeguards aim to detect nuclear material being diverted for malicious purposes in a timely manner. The IAEA defines a significant quantity of nuclear material to be a useful amount of nuclear material for which it would be possible to manufacture a nuclear bomb. The significant quantities of material are 8 kg for plutonium and $^{233}$U, 25 kg of $^{235}$U for uranium enriched above 20%, 75 kg of $^{235}$U enriched below 20%, 10 tons of natural uranium and 20 tons for depleted uranium and thorium [6].

In addition to fissile material and its isotopic content, nuclear forensics considers the overall composition of a material, such as the chemical composition of the matrix encapsulating the fissile material, and elemental signatures of industrial processes (e.g. iron, chromium, chlorine). Isotopic signatures of decay products and fission daughters are also considered because they can contain information on the history of the material, how it was processed or from where it originated [2]. Safeguards measures benefit from having a wide variety of verification techniques and equipment due to the complex nature of the facilities and materials under safeguards.

1.1.2 Current technologies for nuclear material measurements

Current IAEA safeguards technologies and equipment can be broadly separated into four categories: monitoring and surveillance, non-destructive analysis (NDA), destructive analysis and environmental sampling. Containment and surveillance
are used in tandem with nuclear material accounting and includes camera surveillance systems, container seals, sensors, and detectors that monitor material flow and container transport. Although containment and surveillance efforts do not necessarily involve direct measurements of nuclear material, they aid in the effort to ensure that no material is being diverted or is unaccounted for. Numerous NDA systems are used by the IAEA to monitor nuclear materials without physically altering or destroying the material of interest. The main methods of NDA analysis are gamma spectroscopy, neutron counting, spent fuel measurements, and physical measurements (size, weight, volume). The applications for NDA instruments that measure nuclear radiation will be described in more detail.

Gamma spectroscopy is extensively used by the IAEA. The unique gamma ray spectra produced from plutonium isotopes, their decay products, and enriched uranium are used for nuclear materials accounting and verification. The detectors, used to measure these spectra, range from low to high-resolution and measure isotope-specific gamma rays. The relative intensities of peaks in a gamma spectrum can provide ratios for the isotopic composition of the material and the absolute measurement of peak heights can be used to indicate the presence of nuclear material and provide quantitative information [7]. Low resolution gamma detectors are used in safeguards for qualitative determination, or determining the presence of uranium and plutonium in a material sample. High-resolution gamma detectors are used to measure uranium enrichment in structures such as uranium hexafluoride cylinders.

Neutron counting detectors are often used to identify the source of neutrons and provide quantitative information about the fissile material present. Neutron sources include the spontaneous fission of uranium and plutonium, induced fission, and reactions induced by alpha particles. Neutron measurements are commonly used in combination with gamma measurements in order to verify the isotopic abundance of a fuel assembly, providing information on the irradiation history,
initial fuel composition, and reactor history [8].

Table 1.1. General time scales and uncertainties for several methods used to measure isotopic composition of nuclear material [2, 8, 9].

<table>
<thead>
<tr>
<th>Analysis method</th>
<th>Random (% rel. unc.)</th>
<th>Systematic (% rel. unc.)</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha spec.</td>
<td>0.2</td>
<td>0.3</td>
<td>days</td>
</tr>
<tr>
<td>Gamma spec. (low res.)</td>
<td>0.3</td>
<td>0.3</td>
<td>days</td>
</tr>
<tr>
<td>Gamma spec. (high res.)</td>
<td>0.5-2</td>
<td>0.5-2</td>
<td>days</td>
</tr>
<tr>
<td>TIMS</td>
<td>0.1</td>
<td>0.05</td>
<td>wks–months</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>—</td>
<td>0.005</td>
<td>wks–months</td>
</tr>
</tbody>
</table>

Destructive analysis continues to serve an important role in verification. For isotopic analysis, thermal ionization mass spectrometry (TIMS) or inductively coupled plasma mass spectrometry (ICP-MS) are used. Precision and accuracy of 0.05% or better for isotope ratios of 0.05 to 20 can be achieved by TIMS. The precision of ICP-MS can be as low as 0.005% for the detection of trace isotopes.

Destructive analysis techniques require long sample preparation periods that can involve chemical separation to separate atoms from their sample matrix. Additionally, the samples often need to be shipped to laboratories, introducing further delay to analysis times [9]. A summary of the main analytical techniques used in isotopic analysis of nuclear materials and corresponding precision, accuracy, and analysis times for each method are provided in Table 1.1.

Typical timescales of commonly used techniques for isotopic measurements are in Table 1.1. However, new technologies that could potentially meet future safeguard challenges can help fill the gaps in current capabilities. The IAEA has identified LIBS as a novel technology that could be used for identifying materials in the field, process monitoring and analyzing material in hazardous environments (e.g., hot cells, glove boxes), therefore eliminating the need to take swipe samples
1.2 Laser-induced breakdown spectroscopy

Laser-induced breakdown spectroscopy (LIBS) is an optical emission technique that has a potential to meet the challenges associated with nuclear safeguards capabilities. Research in LIBS has grown at high rate since 1960s, although no individual is credited with inventing LIBS. LIBS enables nearly instantaneous material analysis with high spatial resolution and essentially no sample preparation, avoiding lengthy chemical processing to separate the nuclear material from its...
surrounding matrix.

LIBS is advantageous in nuclear applications because it is relatively unaffected by the effects of ionizing radiation unless optical fiber, lenses and probes must be placed in close proximity to areas of high radiation for long periods of time. For example, measurements such as as X-ray fluorescence spectroscopy are affected by the presence of gamma radiation [10]. Furthermore, LIBS can be used to make measurements in high radiation areas where radiation detection systems may experience appreciable losses due to dead time and detector efficiency, and can also be used to measure non-radioactive sources [11]. Liquid, solid, and gas samples can be analyzed using LIBS. However, one limitation of the technique is that it requires the surface of the material to be accessible. Therefore, LIBS is suitable when the surface that is analyzed is exposed and representative of the entire material of interest.

In LIBS, a pulsed laser is focused onto a sample surface, generating a micro-plasma. The light emitted can be collected and analyzed by a spectrometer to provide information on the elemental composition of the sample, and in some cases its isotopic composition. A diagram of a typical setup used in LIBS is shown in Figure 1.1. LIBS has been applied to elemental analysis of nuclear materials and surrogate samples for radioactive material (e.g., cerium in place of plutonium) [12]. The potential to use LIBS analysis for applications to nuclear fuel composition, waste storage and reactor component monitoring has been explored [10, 13, 14]. Experiments have also been conducted to study the effects of pulse duration and pulse shape on uranium spectra [15, 16, 17, 18]. A current interest exists in improving the resolution of LIBS to help make measurements isotopically selective. However, few options exist for LIBS instruments capable of resolving isotope shifts, the relatively small separation of atomic spectral lines from different isotopes of the same element.
1.3 Fabry-Perot spectroscopy

Commonly based on the measurement of element-specific emissions, LIBS has recently been successfully applied to determine the isotopic content of nuclear materials. However, since high spectral resolution is needed for isotopic measurements, large and costly components are typically required. Coupling a relatively inexpensive, compact Fabry-Perot etalon to a conventional spectrometer represents a practical approach for obtaining high-resolution spectra for isotopic measurements. An Fabry-Perot etalon consists of two highly reflecting, semi-transparent mirrors that transmit incident light with a characteristic periodicity in angle and wavelength. A high-resolution LIBS emission spectrum can be reconstructed from the spatially encoded angular pattern of light transmitted through the etalon. Instrumental design and methods of data analysis are important considerations for achieving the high-resolution and low limit of detection in this approach. The choice and layout of optical components impacts the resolution of the system and the data interpretation.

Accurate analysis of the 2-D intensity pattern measured by the instrument is important for measuring profiles of spectral lines. A variety of algorithms has been developed to deconvolve the input spectrum from the interferometric measurement, but they rely on assumptions made about the shape of the source spectrum [19, 20, 21]. Other techniques include analysis in the frequency domain [22]. Direct least squares fitting of 2-D ring images from a single spectral line has also been proposed [23]. Another alternative is data inversion [24, 25], which can be effective in cases where the spectrum is unknown. A reconstruction method, based on similar principles, was refined in this dissertation to interpret the high-resolution spectrum captured by a hybrid interferometric/dispersive spectrometer.
1.4 Challenges in measuring isotope ratios by LIBS

1.4.1 Prior work

The main challenges in making isotopic measurements include the need for high-resolution detectors to resolve the isotope shifts and the physical broadening of emission peak widths in LIBS spectra that could exceed the separation between lines associated with two isotopes. The lineshapes of LIBS peaks are determined by plasma temperature, pressure, and electron density. In LIBS plasmas, Doppler and Stark broadening are the predominant causes of peak broadening and are influenced by the gas environment surrounding the plasma. The physics of broadening will be covered in further detail in Chapter 2.

Isotopic measurements usually require high-resolution spectrometers and temporally gated detectors to resolve the isotope shift. In previous LIBS studies the isotope shift between $^{235}$U and $^{238}$U of 25 pm at the 424.4 nm emission line has been measured. In the study of uranium by Pietsch et al. [27], a 1 m focal length pass spectrometer was used with a single channel detector and a boxcar integrator, operating as a monochromator scanning in 1 pm increments. The measurement was made under 2.67 Pa pressure and is shown in Figure 1.2. Smith et al. measured the 12 pm isotope shift between $^{239}$Pu and $^{240}$Pu at the 594.5 nm emission line, under a 13.3 kPa helium atmosphere, using a 2 m focal length double-pass spectrometer with an intensified charge-coupled device (ICCD) [28]. A laboratory LIBS system has also been used to detect isotopes of uranium and hydrogen, in air at atmospheric pressure, using a 0.55 m focal length Czerny-Turner spectrometer coupled to an ICCD. The individual peaks of the uranium isotopes were not resolved in this study, but the partial least squares method was used to successfully model the differences in spectra to predict the enrichment of uranium samples with different enrichments, shown in Figure 1.3 [29]. Recently, a compact, portable
Figure 1.2. Spectrum from a sample of uranium enriched in $^{235}\text{U}$ (93.5%) [27].

A LIBS system equipped with a high-resolution spectrometer was used to detect the isotopes of uranium, hydrogen, and lithium with careful experimental timing and high-resolution spectrometers. The results are shown in Figures 1.4 and 1.5. Two Echelle spectrometers, the DEMON (LTB Berlin) and EMU-65 (Catalina Scientific Instruments) were compared for detection of five samples of $\text{U}_3\text{O}_8$ at 10, 30, 50, 70, and 93% enrichment for $^{235}\text{U}$. Although the DEMON performed the best in terms of speed and resolution, the smaller size and weight of the EMU-65 is more favorable for a portable system [30].

Isotope analysis of uranium is also made possible by other laser-ablation sampling analysis such as laser-induced fluorescence [31, 32] and laser absorption spectrometry [33, 34]. These methods can achieve individual isotope selectivity. For example, Liu et al. [33] measured the $^{235}\text{U}/^{238}\text{U}$ isotope ratio at 682.0768 nm.
Figure 1.3. Spectrum of uranium from samples of varying enrichments (0.7, 20, and 93% in $^{235}$U) [29]. Although the 424.4 nm emission line is not resolved, partial least squares algorithm was used to accurately reconstruct uranium enrichments with less than 10% relative accuracy.

($-$12.8 pm shift) with laser absorption. Smith et al. [32] used laser-induced fluorescence to distinguish between the uranium isotopes at 683.2719 nm (16.8 pm shift). A disadvantage of these configurations is that multiple lasers and detectors are required for probing and analyzing the plasma plume. With a single laser for sampling and analysis, LIBS is comparatively simpler to implement as a compact, portable technique.

Recently, LIBS capabilities have been extended to include studies of molecular species in the laser-induced plasma [35]. Compared to atomic emission spectra, molecular emission spectra exhibit greater isotope shifts, relaxing the requirements on spectral resolution when performing isotopic characterization of nuclear materials. Laser ablation molecular isotopic spectrometry (LAMIS) was developed to make isotopic measurements from molecular spectra [36, 37, 38, 39]. The rotational and vibrational energies in a molecule can result in much larger isotope shifts for molecular emissions. Boron isotopic ratios have been measured in four
boron carbide samples with a range of $^{10}\text{B}$ enrichments, even without the use of ICCD detectors, which provide temporal gating of several nanoseconds in most LIBS measurements. ICCDs are commonly used to gate out the early broadband continuum emission from the plasma to reduce the signal-to-background ratio. However, it was recently determined that the use of a non-gated detector is sufficient for accurate isotopic characterization with a femtosecond laser [40]. It was further demonstrated that high-fidelity isotopic characterization is possible using a nanosecond laser with a non-gated detector [41, 42]. Molecular emission of boron oxides are shown in Figure 1.6. While the resolution requirement may not
be as stringent, signal-to-background ratio for molecular peaks is often poor and molecular spectra typically require mathematical processing with chemometrics. Furthermore, molecular measurements are limited to those elements that combine to form molecular species. Because molecular rotations and vibrations are mass dependent and isotope shifts scale with the reduced mass of the molecular species, heavier atoms exhibit smaller shifts. A molecular isotope shift in LIBS spectra for uranium has not yet been reported.

![Figure 1.6](image)

**Figure 1.6.** Molecular emission of boron oxides at various $^{10}$B enrichment levels from nanosecond laser pulses [42].

High-resolution spectrometers can be expensive (e.g. Echelle system) and large (e.g. 2-m focal length Czerny-Turner spectrometer). Recently, Effenberger and Scott proposed an alternative method for performing high-resolution LIBS measurements by integrating a low-cost Fabry-Perot etalon with a 0.5 m focal length Czerny Turner spectrometer [43]. The Fabry-Perot etalon is a compact, high-resolution device that separates light of different wavelengths by interference. Bright concentric rings representing constructive interference occur at specific angles relative to the optical axis. When an Fabry-Perot etalon is coupled to an auxiliary dispersion device, such as a grating-spectrometer, a portion of the circular
pattern is further separated laterally, by wavelength, and imaged. High-resolution spectral information is retained in the vertical portion of the 2-D ring pattern. The resolution that can be achieved is determined mainly by the coefficient of finesse of the etalon (which determines the relative width of a transmission band and is independent of the thickness of the etalon) and the incident power on the detector, and not by the resolution of the grating spectrometer. Effenberger and Scott demonstrate instrument performance using the hyperfine doublet of the 313.2 nm mercury emission line, which exhibits a splitting of 29 pm, of similar magnitude to the isotope shift of uranium [43].

1.5 Research objectives

An immediate need exists for rapid, real-time detection, elemental, and isotopic characterization of materials relevant to nuclear safeguards. LIBS is an established technique that can potentially meet the characterization needs with little to no sample preparation. Current barriers to wide implementation of LIBS in nuclear applications include the difficulties in making high-resolution measurements for isotopic characterization.

In this dissertation a high-resolution measurement approach based on an inexpensive and compact Fabry-Perot etalon integrated with Czerny-Turner spectrometer is used [26]. The key contributions in this dissertation are the development of a mathematical reconstruction technique to accurately extract the high-resolution spectrum from the measured data, and the demonstration of isotopically selective LIBS measurements of uranium in ambient air. Although these measurements were made in a laboratory setting, the results of this work could eventually lead to the development of portable, low-cost, and high-resolution LIBS instruments with isotopic-measurement capability.
1.6 Outline of dissertation

In Chapter 2, the properties of laser generated plasmas are discussed. This chapter also introduces the processes responsible for spectral broadening in the measured spectrum, and finally discusses the origin of atomic isotope shifts. Chapter 3 begins with a brief history of spectroscopic measurements, followed by a discussion of different spectrometers and methods commonly used in LIBS. Next, a comparison of the detectors is presented. Chapter 4 begins with a derivation of the analytical model of the instrument, followed by a description about spectral reconstruction methodology. An analysis of the system components is provided in Chapter 5, along with practical considerations for the instrument design to be used for high-resolution measurements. The experimental results are presented in Chapter 6. Chapter 7 provides a conclusion for the dissertation and outlines future work.
Chapter 2

Properties of laser produced plasmas

2.1 Overview

In LIBS, the high irradiance laser pulse focused onto a surface generates a luminous plume of atoms and molecules. The elemental and isotopic analysis is dependent on the emission from a small plasma\(^1\) generated in the interaction of a laser pulse with a surface. The principles of LIBS are similar to those of plasma emission spectroscopy in which a sample is transported to the plasma source in order to excite the atoms of the sample to a higher energy state. In conventional atomic emission spectroscopy, the light emitted from the sample is spectrally resolved to provide qualitative and quantitative information. However, in LIBS the plasma can be generated without moving the sample from its original location or preparing it for analysis. Also, the detector system is protected from contamination of the sample because it detects plasma emission light at some distance from the sample surface and does not need to physically contact the material. One advantage of LIBS is that it does not require a complex arrangement of experimental equipment. The necessary components include the laser, focusing optics, light collection

\(^1\)The LIBS community commonly uses “plasma” to mean a partially-ionized (and not a fully-ionized) plasma. LIBS can simultaneously detect emission from free electrons, atomic ions, neutral atoms, molecular ions and neutral molecules.
optics, spectrometer or dispersion device, timing controller, detector, and method of collecting data.

Emission by the LIBS plasma generated by a short laser pulse varies with time. The laser pulse is focused using a lens. The spot size, and hence the irradiance, depends on the wavelength of the laser, the size of the unfocused laser beam, and the focal length of the lens. Assuming a Gaussian beam shape and perfect beam quality, the focal spot size is approximately

\[ W_{\text{spot}} \approx \frac{\lambda}{\pi W_0^2 f}, \]  

(2.1)

where \( W_{\text{spot}} \) is the beam waist radius at the focal plane of the lens, \( W_0 \) is the input beam radius, \( f \) is the focal length of the lens, and \( \lambda \) is the wavelength of the laser. The irradiance of the focused beam can be calculated using

\[ I \approx \frac{E}{\tau \pi W_0^2}, \]  

(2.2)

where \( E \) is the laser pulse energy and \( \tau \) is the pulse duration [44]. The peak power of the laser needs to be sufficiently high to produce material breakdown. Focusing the laser to a spot size a few tens of micrometers in diameter on the sample can be used to reach typical breakdown irradiance thresholds \((10^8 - 10^{12} \, \text{W cm}^{-2})\), depending on wavelength and duration of the laser pulse [45]. The discrete lines in plasma emission are due to recombination or de-excitation of atoms and ions to lower energy states [46].

\[ M^+ + e^- \rightarrow M + h\nu \quad \text{(recombination)} \]  

(2.3)

\[ M^{++} \rightarrow M^+ + h\nu \quad \text{(de-excitation of ions)} \]  

(2.4)

\[ M^* \rightarrow M + h\nu \quad \text{(de-excitation of atoms)} \]  

(2.5)
where $M$ represents a neutral, $M^+$ is an ion, $^*$ indicates an excited state, $e^-$ is an electron, $h\nu$ is the photon energy where $h$ is Planck’s constant and $\nu$ is the photon frequency.

Emitted light is collected by lenses or a fiber optic cable and transmitted to the spectrometer. A spectrum is measured by integrating the optical signal on the detector over a time window set to coincide with the lifetime of the plasma. The emitted light from transition energy levels for different atoms and molecules provide unique spectral fingerprints that can be used for material analysis [47].

### 2.2 Physics of laser-induced plasmas

#### 2.2.1 General properties

The formation of the plasma during laser ablation is the first stage in LIBS, and affects the resolution, accuracy, sensitivity, and precision of the analysis. The formation and expansion of the laser-induced plasma is time dependent and can be broken down into different stages. The following discussion is primarily focused on the physics of laser-induced plasmas of solid samples. First, the ablation process begins with the laser interacting with the material. The heating, ionization, and vaporization a surface undergoes is highly dependent on the sample material, laser irradiance, and pulse duration. When the plasma forms it expands perpendicular to the surface, continuing to expand after the end of the laser pulse. The electron density, temperature, and speed of the expanding plasma depend on the laser ablation process. After the laser pulse terminates, plasma expansion is determined by the plasma properties and interactions with the ambient environment (i.e. air, vacuum, or gas). Understanding the plasma expansion is important to LIBS measurements. In the early stage of the plasma formation, a high density of free electrons and ions is present. Spectral broadening is mainly due to the Stark broadening. As recombination begins to occur later in the plasma lifetime,
electron density decreases and becomes the main contributor to spectral broadening. Lastly, particles will be formed from condensation of the plasma gas and ejected by the high pressure gradient of the expanding plume. A summary of the laser ablation processes is shown in Figure 2.1 and is described in detail in the following section. Most temporal LIBS spectra are taken nanoseconds to microseconds after the laser pulse is incident the sample, which allows the spectra to be optimally measured [47, 48].

Material properties affect ablation and vaporization of the sample. The scattering, transmission, absorption, and thermal conductivity influence the laser-material interaction. Materials with high absorptivity for the laser wavelength are ablated more efficiently and create clean ablation craters. The laser pulse coupling to transparent materials is less efficient, generating irregularly shaped ablation craters. Thermal conductivity determines heating around the ablation spot because the amount of material evaporated depends on the material’s boiling point at a given pressure. Therefore, crater size and shape are affected by the incident laser irradiance [49].

The chemical composition of the target material can also affect ablation. For example, reactive metallic samples such as uranium readily oxidize in ambient air, primarily in the presence of water vapor. The potential for oxide overgrowth on the uranium metal surface is high due to the reactivity of the actinide elements [50]. Precautions need to be taken to reduce or account for the effects of the material surface, a mixture of oxidized and reduced uranium, since oxygen accumulated at the surface can saturate the emission from uranium. LIBS is unique because the process of laser ablation can also be used to clean oxidized surface prior to analysis [51].
2.2.2 Ablation process

The ablation process occurs when the laser pulse interacts with the sample surface to break bonds and generate an ionized gas. The plasma is ignited and sustained primarily through inverse bremsstrahlung heating, from collisions between ablated atoms, electrons, ions, and surrounding gases. Inverse bremsstrahlung occurs when an electron absorbs photons from the laser pulse and collides with neutrals. Ionization occurs when electrons are imparted with energy greater than the ionization potential of the gas. If the electron gains sufficient energy, it can ionize neutrals and cause cascaded ionization, increasing the electron population exponentially with time. The reaction is described as

$$M + e^- \rightarrow M^+ + 2e^- \text{ (cascade ionization)}.$$

Another mechanism, which is predominant at shorter wavelengths, is multiphoton ionization. This process occurs when an atom or molecule simultaneously absorbs a sufficient number of photons to become ionized. During multiphoton ionization,
simultaneous absorption of multiple photons exceeds the ionization energy, or the energy required to excite a valence electron to the conduction band, described by the reaction

\[ M + m\hbar\nu \rightarrow M^+ + e^- \text{ (multiphoton ionization)}, \]

(2.7)

where \( m \) is the number of photons needed to exceed the ionization potential [52]. There are many factors that influence plasma ablation, such as laser wavelength, pulse duration, energy, and ambient conditions surrounding the plasma. These in turn influence the energy that atoms and ions acquire. Additional heating of the plasma can occur if the laser pulse duration is long enough to cause additional heating after the onset of plasma formation. Mechanisms of bond-breaking vary for different pulse durations and irradiances. For nanosecond pulses, ablation primarily involves thermal processes such as melting, sublimation, vaporization, and ionization. The laser pulse increases the surface temperature of the sample, leading to melting and vaporization. During nanosecond ablation the plasma can experience plasma shielding, which involves heating of the plasma by the later end of the laser pulse, significantly affecting vaporization and plasma properties.

Compared with nanosecond pulses, femtosecond pulses nearly fully ionize the target (at typical irradiances of \(10^{13}–10^{14} \text{ W cm}^{-2}\)), leading to improved ablation precision and lower background from continuum emission [53]. Following ablation of the sample, the emission from plasma consists of several contributions, including the continuum background from bremsstrahlung, recombination and cooling. The pulse duration of a femtosecond pulse is shorter than electron thermalization time in a solid sample, which undergoes plasma formation directly with minimal thermal conduction. Plasma shielding is negligible in femtosecond ablation. The rapidly cooling plasma does not undergo significant interactions with the tail of the laser pulse, which decreases the magnitude of continuum emissions compared to those when longer pulse duration are used [54].
The plasma expands outward at supersonic speeds into vacuum or gas. Plasma evolution depends on the laser irradiance, wavelength, focal spot, target material, surrounding gas and surrounding pressure. The expansion of the hot vapor occurs when an ionized vapor plume, with a higher pressure than its surroundings, is formed. As the high pressure vapor expands it transfers energy to the surroundings through thermal conduction, radiative transfer, and compression heating that drives the shock wave. The gas adjacent to the shockwave of the plume is heated and enables the absorption of laser radiation, when the cold atoms would have otherwise been transparent to the laser pulse. The gas layer rapidly heats to plasma conditions when a sufficient ionization has occurred. The absorbing gas layers of the shockwave change the plasma from a confined vapor to a strongly absorbing plasma that absorbs the remainder of the laser energy [55, 56].

The final stage of laser-produced plasma is nanoparticle formation, which occurs microseconds after the initiation of ablation. Particles can be formed by condensation, sample ejection or exfoliation. Particle chemical composition varies with particle size, which depends on laser energy, laser pulse duration, ambient gas and sample composition. Although particle formation is important for techniques such as inductively coupled plasma spectroscopy, they can be detrimental to LIBS because the particles are not useful for analysis. The particles can be evaporated by the expanding plasma plume or re-evaporated by a second laser pulse [48].

2.2.3 Detection of plasma emission

Laser-induced plasmas are time dependent and have continuum and line emissions. Continuum radiation is emitted because of free-free transitions or photo-ionization (bound-free transitions) occurring in the plasma. Free-free transitions occur when a photon is absorbed by a free electron moving in the electric field of an ion. The electron is initially excited to a higher energy state. The de-excitation of the electron emits bremsstrahlung, which contributes to the continuum emission
from atomic ionization. Photoionization, or bound-free transitions, occurs when an electron gains enough energy to rise from its ground state to an excited state. During bound-free transitions, the energy of the electron can range from zero to high energy (larger than the ionization energy). The inverse of photo-ionization and recombination also contribute to the total continuum radiation from atomic processes. Non-thermal electrons do not contribute to the continuum emission because recombination cross sections are negligible for electrons with low kinetic energy [55, 57]. Line emission, or bound-bound transitions, corresponds to the
energy between two discrete energy states. Individual line emissions are narrow because they each exist within a very small energy range.

The early phase of plasma formation, the plasma emits continuum radiation, which remains near the ablation spot. As the plasma expands and cools, the emission of discrete spectral lines is observed. Spectral lines from highly ionized atoms are observed closer to the center of the plasma and lines from neutral emissions occur in the outer, cooler regions of the plasma plume. When using a detector to integrate spatially over the entire plasma plume, the characteristic line emissions are superimposed with continuum emission. Continuum emission decays faster than line emissions. Discrete line emission, which is used to identify material composition, becomes prominent as the continuum emission subsides [55]. Figure 2.2 depicts a typical history of a laser-generated plasma light signal. Often, the emission signal is recorded after a time delay after the laser ablation event to separate the discrete lines from the broadband continuum light from the LIBS plasma.

2.3 Plasma emission characteristics

2.3.1 Plasma parameters

In LIBS, certain plasma parameters are important to take into account when making spectral measurements. These include electron density, plasma temperature, spectral line strengths, and spectral profiles. Electron density influences peak broadening and high density plasma can cause self-absorption. Evaluation of plasma temperature and electron density are connected to the concept of thermodynamic equilibrium.

Local thermodynamic equilibrium (LTE) is one of the figures of merit for quantitative LIBS measurements. Whether a plasma exists in local LTE depends on plasma temperature and electron density. For a plasma to be in thermodynamic equilibrium, all processes are characterized by a single temperature. For LTE, the
electron distribution needs to be described by a Maxwell-Boltzmann distribution, and is justified if the time it takes for the plasma to expand exceeds the time it takes the system to reach a new equilibrium (relaxation time).

The plasma temperature can be determined because of the Boltzmann factor [58]. The Saha equation is used to determine the temperature of the plasma from the ratio of the ion and neutral lines:

$$\frac{I_{\text{ion}}}{I_{\text{atom}}} = \frac{2(2\pi k T)^{3/2}}{N_e h^3} \left( \frac{gA}{\lambda} \right)_{\text{ion}} \left( \frac{\lambda}{gA} \right)_{\text{atom}} \exp\left[-\frac{(V^+ + E_{\text{ion}} + E_{\text{atom}})}{kT_{\text{ion}}} \right],$$  \hspace{1cm} (2.8)

where $I$ is the integrated emission strength, $N_e$ is the electron density, $gA$ is the product of the statistical weight and the Einstein coefficient for spontaneous emission of the upper energy level, $\lambda$ is the wavelength, $T_{\text{ion}}$ is the ionization temperature, $V^+$ is the ion potential of the atom, $E$ are the excitation energies of the ionic or atomic line, $k$ is the Boltzmann constant, and $h$ is Planck’s constant. The Boltzmann factor is used to calculate plasma temperatures for neutral to neutral lines:

$$\frac{I_1}{I_2} = \frac{g_1 A_1 \lambda_2}{g_2 A_2 \lambda_1} \exp\left[-\frac{E_1 - E_2}{kT_e} \right],$$  \hspace{1cm} (2.9)

where $I$ is the integrated emission for the pair of neutral lines. Accuracy of this approximation increases with the number of lines used and with the energy difference between the two lines [55, 59].

If the plasma density is high, the plasma absorbs a portion of the light that it emits. Self-absorption distorts the spectral line profile and can lead to line broadening; it occurs mainly for transitions between resonance lines and the ground state. To verify that the plasma is not optically thick for lines to be used for quantitative analysis, the ratios predicted by the statistical weights of upper energy levels should be verified with experimental observation. There is a tendency for spectra of solid samples with high analyte concentrations or high laser irradiance
to exhibit self-absorption [55].

2.3.2 Spectral line features

The profile of a spectral line is affected by the sample material and the gas environment surrounding the plasma. Several line broadening mechanisms occur in a LIBS plasma. Stark broadening is dominant when emitting species experience an electric field due to high electron density. Doppler broadening occurs due to thermal motion of emitting ions. The instrumental broadening effects of the spectral apparatus used in the LIBS measurement is also pertinent when considering line broadening mechanisms [58]. Natural line broadening is a result of the finite lifetime of the excited states, but is negligible in LIBS plasmas.

2.3.2.1 Stark broadening

During early stages of plasma formation the electron density is high, on the order of $10^{15} - 10^{18}$ cm$^{-3}$, which can cause Stark broadening. Stark-broadened spectral lines are described by Lorentzian distributions, with a central wavelength that can be red- or blue-shifted. A red shift (to a longer wavelength) is defined to be positive; conversely, a blue shift (to a shorter wavelength) is defined to be negative. In spectroscopy, linear and quadratic Stark effects have been observed. The linear Stark effect primarily describes hydrogen atoms, which exhibit a full width half maximum (FWHM) described by

$$N_e = C \Delta \lambda^{3/2},$$

(2.10)

where $C$ is a tabulated constant and $\Delta \lambda$ is the FWHM of the emission. For plasma measurements of non-hydrogen atoms, the quadratic Stark effect represents the broadening of transitions of neutral atoms or singly ionized ions. The term, quadratic Stark effect, is used because the change of emission frequency is
proportional to the square of the electric field strength. This arises because multi-electron species have an induced dipole moment due to the external electric field. The FWHM of a Stark-broadened line is approximately

\[
\Delta \lambda_S = \left[ 1 + 1.75A \left( 1 - \frac{3}{4}N_D^{-1/3} \right) \right] W \left( \frac{N_e}{10^{16} \text{ cm}^{-3}} \right),
\]

(2.11)

where \( A \) is a dimensionless coefficient, \( N_D \) is the electron density in the electrostatic Debye sphere, \( N_e \) is the number of electrons, and \( W \) is the Stark broadening parameter. The equation is usually reduced to

\[
\Delta \lambda_S = W \left( \frac{N_e}{10^{16} \text{ cm}^{-3}} \right),
\]

(2.12)

assuming that that ionic contributions are small.

### 2.3.2.2 Doppler broadening

Doppler broadening, the dominant mechanism at low electron densities, occurs because thermal motion of atoms or molecules causes the observed frequency to change. Particles traveling at different velocities can be red or blue-shifted. Doppler broadening is described by a Gaussian profile. The FWHM of a spectral line is

\[
\Delta \lambda_D = \left( \frac{8kT \ln 2}{M_a c^2} \right)^{1/2} \lambda_{ij0},
\]

(2.13)

where \( M_a \) is the mass of the emitting atom species, \( kT \) is the product of the Boltzmann constant and the thermodynamic temperature, and \( \lambda_{ij0} \) is the center wavelength of the transition from \( j \) to \( i \). Doppler broadening plays a role in LIBS after the plasma has expanded and cooled. At this point the electron densities are low and Stark broadening is reduced.

When Stark and Doppler effects both contribute to broadening of LIBS spectra,
the Voigt profile is used to describe the line profile. The Voigt profile is defined as

\[
\Gamma (\lambda) = \frac{2}{\Delta \lambda_D} \sqrt{\ln 2} \frac{K (u, a)}{\pi},
\]  

which is a convolution of a Lorentzian and a Gaussian profile.

\[
K (u, a) = \frac{a}{\pi} \int_{-\infty}^{+\infty} e^{-t^2} \frac{e^{-(u-t)^2}}{(u-t)^2 + a^2} dt
\]  

and

\[
u = \frac{2\sqrt{\ln 2}}{\Delta \lambda_D} (\lambda - \lambda_{ji0}),
\]

\[
a \approx \sqrt{\ln 2} \frac{\Delta \lambda_S}{\Delta \lambda_D},
\]

where \( a \) is approximated by assuming that natural line width broadening is negligible. \( \Delta \lambda_S \) is the Lorentz width due to Stark broadening, and \( \Delta \lambda_D \) is the Doppler line width [59, 60] A comparison of a Gaussian, Lorentzian, and Voigt profiles is shown in Figure 2.3.

**Figure 2.3.** The Voigt profile (green) is a convolution of the Lorentzian (red) and a Gaussian peak (blue).
2.3.2.3 Instrumental broadening

Measured spectral line profiles are usually a combination of the instrument resolution and the different plasma parameters. Therefore, the instrumental contribution should be removed when extracting plasma parameters from measured spectral lines. Instrument functions are unique for each spectrometer and depend on the slit width, grating dispersion, and the detector. A typical wavelength spectrometer slit-function can be estimated by a Lorentzian or a Gaussian profile. Assuming that Stark broadening is the dominant mechanism in LIBS measurements, there are two methods for deconvolving the instrument function of the spectrometer. If both the Stark and instrument profiles are assumed to be Lorentzian functions, the linear summation applies for the measured width:

$$\Delta \lambda_m = \Delta \lambda_S + \Delta \lambda_i,$$

(2.18)

where $\Delta \lambda_i$ is the instrumental width. Under these assumptions, the actual line width can be obtained by the difference between the measured and the instrument widths [55]. However, a different approach is needed when the instrument broadening is modeled by a Gaussian function. Then, the measured spectral width is described by

$$\Delta \lambda_m = \Delta \lambda_S/2 + \sqrt{\left(\Delta \lambda_S/2\right)^2 + (\Delta \lambda_i)^2},$$

(2.19)

but the actual line width is not retrieved by linear subtraction. Because the measured width is a convolution of the Stark-broadened and the instrument-broadened widths, a deconvolution procedure should be employed. For a grating spectrometer, bandwidth is a function of wavelength and needs to be taken into account. At the end of the plasma lifetime, when plasma broadening contributions become minimal compared with contributions from the instrument, the spectrometer slit function can be obtained directly from the spectral line [58].
2.4 Isotope shifts in atomic spectra

Atomic spectral lines are characteristic of the emitting species and are isotope dependent. Energy differences between emission from different isotopes are referred to as the isotope shift, and occur in molecular and atomic spectra. The energy of a photon from an atom is

$$\Delta E = E_2 - E_1 = h\nu,$$  \hspace{1cm} (2.20)

where $E_2$ and $E_1$ are atomic energy levels. The transition energies for atoms of different masses, but the same atomic number, are

$$\Delta E' = E'_2 - E'_1 = h\nu' \text{ and } \Delta E'' = E''_2 - E''_1 = h\nu'', \hspace{1cm} (2.21)$$

and the isotope shift is

$$IS = \Delta E'' - \Delta E' = (E''_2 - E''_1) - (E'_2 - E'_1). \hspace{1cm} (2.22)$$

Excitation and ionization of different isotopes of an element vary due to isotope shifts and hyperfine splitting. Isotopes with odd atomic mass number exhibit hyperfine structure, which is the splitting of energy states caused by magnetic hyperfine interaction. The nucleons in isotopes with an even mass number are paired, resulting in a zero total angular momentum, $I$. Nuclei with an odd mass number have one unpaired nucleon and a non-zero angular momentum, which couples with the angular momentum, $J$, of the electrons around the nucleus. The total angular momentum of the atom is $F = I + J$ and the total number of magnetic substates is equal to $(2J + 1)(2I + 1)$. The nuclear spin angular momentum for isotopes with odd mass number is $I = 1/2$, which results in splitting of the upper energy levels. For an isotope with even mass number there is a single lower energy sublevel and three magnetic substates in the upper level.

The hyperfine structure energy levels are affected by isotope shifts, which are
dominated by two effects: the field shift and the mass shift. The mass shift is a major contributor to the isotope shift for light isotopes. The mass-dependent isotope shift is due to the differences in the reduced mass,

\[
m_r = \frac{m_e m_n}{m_e + m_n},
\]

(2.23)

of a bound electron that alters the energy of its excited states, where \( m_n \) is the nuclear mass, and \( m_e \) is the electron mass [61].

Heavier atoms exhibit a shift in addition to the mass shift due to the volume of the nucleus. Adding more neutrons to the nucleus changes its charge distribution and the energy of the orbiting electron. This is known as the field shift, or the volume shift, and is due to the size and shape of the nucleus; the resulting electric charge distribution affects the position of atomic energy levels. The change in energy for an electron is

\[
d\Delta E = \int_0^{r_0} \rho_e (r) \delta \Delta V 4\pi r^2 dr,
\]

(2.24)

for two different isotopes, where \( \delta \Delta V \) is the potential difference, \( \rho_e (r) \) is the charge density, and \( r_0 \) is the radius of the nucleus.

Because proton distributions for different isotopes exhibit distinct charge distributions, the change in atomic energy levels are due to the shapes of the electric field [62]. For LIBS, it is necessary for the linewidth to be narrower than the isotope shift in order for the shift to be resolved. Stark and Doppler broadened spectral lines can exceed this limit [36].
Methods of spectroscopic measurements

3.1 Overview

A spectrometer is a central component of every LIBS system and its proper selection and operation is crucial for successful spectral characterization. Spectrometers are used to spectrally disperse the emission from the plasma in order to resolve spectral lines. The types of spectrometers mainly used in LIBS are Czerny-Turner and echelle spectrometers. Interferometric methods are also used in spectroscopy. The resolving power of interferometers can be superior to large spectrometers, but interferometric methods are not commonly used for measurements of LIBS spectra. Interferometers are widely used in stabilizing laser wavelengths and measuring laser line widths. This chapter describes the methods of spectroscopic measurements in LIBS, their principles of operation, and provides a comparison to interferometric approaches.
3.2 Czerny-Turner spectrometers

In grating spectrometers, a reflecting diffraction grating is usually used. In a Czerny-Turner spectrometer, light passes through an entrance slit and is collimated by a concave mirror onto a diffraction grating. The dispersed light is brought back to focus on the detector plane by a second concave mirror. The detector can be a segmented camera array (CCD, ICCD) or a single-pixel detector (photodiode or photomultiplier tube). Segmented detectors allow simultaneous measurements of a range of wavelengths, obtaining a spectral profile. A monochromator arrangement that uses a single-pixel detector can record an interval of wavelengths with high resolution by making a scanning measurement. A representative diagram of the Czerny-Turner configuration is shown in Figure 3.1.

Diffraction gratings have grooves parallel to the entrance slit of the spectrometer. The coherent superposition of waves diffracted from the grating results in a coupling of a specific spectral component to an angle. For a beam of light incident at angle $\alpha$ from the normal to the grating plane, constructive interference is
obtained for light reflected with an angle $\beta$ for which

$$\sin \alpha + \sin \beta = m\lambda/d, \quad (3.1)$$

where $m$ is the diffraction order, $d$ is the distance between two adjacent grooves on the grating, and $\lambda$ is the wavelength. This relationship is known as the grating equation. Angles are measured on the same side of the normal to the grating. When two parallel monochromatic beams are diffracted by a grating, they experience angular deviations relative to the direction normal to the grating. The angular separation $\Delta \theta$ of two different wavelengths is

$$\Delta \theta = \left( \frac{d\beta}{d\lambda} \right) = \frac{m d}{d \cos \beta}, \quad (3.2)$$

where $d\beta/d\lambda$ is the angular dispersion. The linear dispersion for central wavelength $\lambda$ of order $m$ corresponding to an angle of diffraction $\beta$ is the product of the angular dispersion and the focal length of the system:

$$f \Delta \theta = f \frac{d\beta}{d\lambda} = \frac{mf}{d \cos \beta}, \quad (3.3)$$

where the dispersed light is brought to focus at focal length $f$, the focal length of the exit mirror. The unit for linear dispersion is typically reported in Å mm$^{-1}$. The wavelength range seen by the detector depends on the size of the array and is equal to the linear dispersion times the size of the array along the dispersion axis. The minimum $\Delta \lambda$ resolvable depends on the spectral profile and the ratio between the intensity distributions of the two lines. The spectral resolution is limited by the slit width, detector sampling, and optics.

Many spectrometers are arranged such that $\alpha = \beta$, which is known as a Littrow
condition. For this arrangement, the grating equation is simplified to

\[ 2d \sin \alpha = m \lambda, \]  

(3.4)

and the theoretical resolving power of the spectrometer is

\[ R = \frac{N d (\sin \alpha \pm \sin \beta)}{\lambda}, \]  

(3.5)

which simplifies to

\[ R = \frac{\lambda}{\Delta \lambda} = m N \]  

(3.6)

for a Littrow arrangement. In these equations \( m \) is the diffraction order and \( N \) is the number of illuminated grooves. However, the theoretical resolving power does not take into account the finite slit width of the spectrometer or the diffraction caused by the limiting aperture. The resolution that is achievable in practice is approximately three times lower [63].

The sampling frequency of the detector also has an influence on resolution. The Nyquist criterion states that the sampling frequency must be at least twice the highest frequency contained in the signal. Therefore, there needs to be at least two pixels per spectral line; otherwise, the pixel size of the detector is the resolution limiting component.

### 3.3 Echelle spectrometers

Echelle spectrographs are similar to Czerny-Turner spectrographs, except that the gratings use grooves that have a larger space \( d \) between adjacent grooves to achieve diffraction of very high orders. Furthermore, echelle systems use two dispersive components instead of one, such as a grating-prism pair to disperse the spectrum in two dimensions. The spectral information is contained in the dispersed light pattern with multiple orders of diffraction (ranging from 10 to over 100), which
Figure 3.2. Diagram of a typical echelle spectrograph and its components [64].

is imaged onto a two dimensional imaging array. The resolving power is very high according to Equation (3.6), but a small free spectral range exists between adjacent orders. A diagram of a setup is shown in Figure 3.2. The echelle spectrometer can disperse a broad spectral range, usually 100 – 1000 nm. Spectra are recorded for different orders simultaneously and result in a dense pattern of lines and diffraction orders. The complex pattern usually requires sophisticated algorithms to reconstruct the wavelength spectrum from the acquired image [64].

3.4 Fabry-Perot interferometer

The capabilities of the Fabry-Perot interferometer have long been utilized. For example, interferometers can accept irradiances ~100 times larger than a spectrograph of comparable size and resolution. The key principle is that Fabry-Perot light collection is not geometrically limited by a narrow entrance slit as the
Figure 3.3. Diagram of a Fabry-Perot interferometric setup showing the formation of fringes in the focal plane by a lens by light at equal incident angles, where $f$ is the focal length of the fringe-forming lens.

spectrograph. This advantage over grating and echelle spectrometers have been put to practice in astronomical applications because even a relatively compact Fabry-Perot interferometer can provide superior resolution than a large grating with the ability to maximize the light collection of the telescope [65].

Fabry-Perot interferometry has been applied broadly in atomic spectroscopy for measurements of wavelength, hyperfine and isotope shifts of line spectra, and line broadening. Different measurements can be made using this technique. The obtainable spectral information is derived from the equation

$$2nD \cos \theta = m\lambda,$$

where $\lambda$ is the wavelength of the transmitted beam, $D$ is the distance between the mirrors, $n$ is the refractive index of the medium inside the etalon (i.e., air) and $\theta$ is the refracted angle relative to the normal plane of the etalon optics. Uranium isotope ratios have been successfully recorded by pressure scanning methods using Fabry-Perot interferometry and continuous lamp sources [66, 67, 68].

When the interferometer is constructed with a fixed geometric spacing between the end mirrors, the device is known as an etalon. The primary spectroscopic variable is $\theta$ for an etalon configuration, in which the fringes are detected and
imaged in the focal plane of the focusing lens, as shown in Figure 3.3. The resulting image is of the angular radii of successive bright rings. Imaging the pattern is useful for applications in which the measurement involves the distance between closely spaced spectral lines or accurate wavelength measurements by comparison to a known standard. The total transmitted intensity for a plane-parallel Fabry-Perot etalon is described by the Airy equation:

\[ T(\theta, \lambda) = \left( 1 + F \sin^2 \left( 2\pi \frac{D n}{\lambda \cos \theta} \right) \right)^{-1}, \]  

(3.8)

where \( F \) is the coefficient of finesse of the etalon \( (F = 4R/(1 - R)^2) \). The cumulative reflection of the two mirrors is commonly represented by \( R = r^2 \), and \( r \) is the reflectivity of each of the end mirrors of the etalon. \( R \) is usually tabulated as \( R_e \), the effective reflectivity, which takes into account the defects of the etalon optics. The ratio of the separation of adjacent fringes to the FWHM of each peak is a figure of merit known as the finesse, defined as

\[ \mathcal{F} = \frac{\pi \sqrt{F}}{2}. \]  

(3.9)

As the finesse increases, the width of the peak decreases while the transmission intensity of the peak increases. The resolving power is

\[ \mathcal{R} = \frac{\lambda}{\Delta \lambda} = \frac{m\pi \sqrt{F}}{2} = m\mathcal{F}, \]  

(3.10)

where \( m \) is the fringe order and \( \Delta \lambda \) is the least resolvable wavelength difference. The minimum resolvable wavelength, the FWHM, and the finesse are all related to the free spectral range (FSR). The FSR is defined as the length between adjacent orders of constructive interference and is related to the spectral resolution by

\[ \text{FWHM} = \frac{\text{FSR}}{\mathcal{F}}. \]  

(3.11)
The angular dispersion of the Fabry-Perot interferometer is

\[ \frac{d\theta}{d\lambda} = \frac{m}{2nD\sin \theta}, \]  

and the linear dispersion of the ring pattern is

\[ \frac{dD}{d\lambda} = f \frac{d\theta}{d\lambda}, \]  

where \( f \) is the focal length of the focusing lens. The linear dispersion of a Fabry-Perot ring pattern is of at least one order of magnitude greater than the dispersion of a comparable spectrometer, but the free spectral range is small. In applications to spectrometry, spectral isolation of the lines of interest is necessary. This can be accomplished by using a grating spectrograph as a premonochromator, a tandem multietalon spectrometer setup, or a Fabry-Perot setup with auxiliary Littrow mounted grating spectrometer. A configuration where a grating spectrometer is used to provide auxiliary dispersion is shown in Figure 3.4.

\[ d\theta \quad dD \quad \frac{d\theta}{d\lambda} \quad \frac{d\theta}{d\lambda}, \]

\[ \text{where } f \text{ is the focal length of the focusing lens. The linear dispersion of a Fabry-Perot ring pattern is of at least one order of magnitude greater than the dispersion of a comparable spectrometer, but the free spectral range is small. In applications to spectrometry, spectral isolation of the lines of interest is necessary. This can be accomplished by using a grating spectrograph as a premonochromator, a tandem multietalon spectrometer setup, or a Fabry-Perot setup with auxiliary Littrow mounted grating spectrometer. A configuration where a grating spectrometer is used to provide auxiliary dispersion is shown in Figure 3.4.} \]

\[ \text{Figure 3.4. Experimental setup showing an Fabry-Perot coupled to a secondary dispersion, Littrow mounted grating spectrometer, used by Effenberger [43].} \]

However, real etalons are not perfect. The actual finesse of the etalon is lower...
than the previously defined finesse $\mathcal{F}$, which only takes into account losses due to reflections and is referred to as the reflectivity finesse $\mathcal{F}_R$. The additional defects that limit performance of real etalons include spherical defects, spherical irregularities, and parallelism defects, illustrated in Figure 3.5. The total defect finesse is

$$\frac{1}{\mathcal{F}_d} = \sqrt{\left(\frac{1}{\mathcal{F}_S}\right)^2 + \left(\frac{1}{\mathcal{F}_{dg}}\right)^2 + \left(\frac{1}{\mathcal{F}_{dp}}\right)^2}.$$  \hspace{1cm} (3.14)

The value often reported by manufacturers is the effective finesse, $\mathcal{F}_e$, which takes into account the imperfections of the etalon.

![Graphical representation of defects contributing to the total defect finesse of the etalon: parallelism defects $\mathcal{F}_{dp}$ (a), spherical defects $\mathcal{F}_S$ (b), surface irregularities $\mathcal{F}_{dg}$ (c).](image)

The effective finesse of the etalon is

$$\frac{1}{\mathcal{F}_e} = \sqrt{1/\left(\mathcal{F}_R\right)^2 + \left(1/\mathcal{F}_D\right)^2 + \left(1/\mathcal{F}_\theta\right)^2 + \left(1/\mathcal{F}_S\right)^2},$$  \hspace{1cm} (3.15)

where $\mathcal{F}_e$ is the reflectivity finesse, $\mathcal{F}_D$ is the diffraction limited coefficient of finesse, $\mathcal{F}_\theta$ is the incident beam divergence coefficient of finesse, and $\mathcal{F}_S$ is the deviation due to spherical aberration.

$$\mathcal{F}_R = \frac{\pi \sqrt{R}}{1 - R}$$  \hspace{1cm} (3.16)

$$\mathcal{F}_S = \frac{M \lambda}{2 \lambda_0}$$  \hspace{1cm} (3.17)
\[ \mathcal{F}_\theta = \frac{\lambda}{D \tan^2 \theta} \]  
(3.18)

\[ \mathcal{F}_D = \frac{CA^2}{2D\theta}. \]  
(3.19)

\(M\) is the beam parameter, \(CA\) is the clear aperture, and \(\lambda_0\) corresponds to the wavelength at which the value for the reflectivity \(R\) is reported [69].

3.5 Spectrometers used for LIBS: a comparison

The different spectrometers used in LIBS have distinct advantages and drawbacks. Czerny-Turner spectrometers are most commonly used to measure LIBS plasma. However, they are inherently limited in spectral range and require long focal lengths in order to achieve high resolution. This requires a larger instrument housing to accommodate optics and the path lengths that light of different wavelengths need to travel in order to be sufficiently separated laterally. As a result, a smaller fraction of the collected light is detected.

The main advantages of echelle spectrometers are their high resolution and ability to collect a single spectrum encompassing a wide spectral range spanning hundreds of nanometers. Moreover, they are compact and have few moving parts. The resolution and sensitivity of the echelle spectrometer varies with wavelength, due to dispersion. Dispersion also causes losses of the spectrum located between different orders. Dynamic range is also important to consider because saturated pixels of the detector can cause electrons to diffuse to adjacent pixels, causing false lines to appear [70].

Compared to conventional spectrometers, Fabry-Perot interferometers have superior resolving power and are inexpensive and compact. However, because multiple reflections are involved in a measurement, Fabry-Perot optics have stricter requirements for optical quality than their counterparts in other instruments (i.e., gratings). Distortions of wave fronts after many reflections from an imperfect
surface accumulate, leading to a reduction in resolution because of transmission peak broadening [65].

Most spectroscopy applications with the Fabry-Perot interferometer involve scanning measurements over the spectral range, but the plasma light emitted in LIBS is short-lived and thus requires direct imaging of the interference fringes per spectral recording. For typical laser linewidths, optical filters suffice for isolating relevant wavelengths. However, LIBS spectra have lines of many different wavelengths and require a secondary method for auxiliary dispersion of the dense ring pattern, such as a Littrow mounted grating spectrometer. There is also a tradeoff between spectral resolution and sensitivity. The first LIBS measurements made using a Fabry-Perot etalon coupled to a spectrometer required accumulated emission from hundreds of laser shots in order to obtain a sharp ring image [26].

A direct comparison of spectrometers may not be valid. One needs to compare the combined performance of the detector and spectrometer. By doing so, one would be solely comparing the LIBS plasma and not a combination of the plasma emission and experimental instrumentation [71]. The selection of the spectrometer-detector combination depends on the types of measurements to be made because there is often a tradeoff between wavelength coverage, spectral resolution, read-out time, dynamic range, and limits of detection [72]. Other aspects of the system, such as the cost, size, and portability, should also be considered for the selection of LIBS detector systems.
4.1 Introduction

Accurate analysis of the 2-D fringe pattern measured by the instrument is important for interpreting profiles of spectral lines. A variety of algorithms have been developed to deconvolve the input spectrum from the interferometric measurement, but they rely on assumptions made about the shape (e.g., Gaussian, Lorentzian, Voigt functions) of the source spectrum [19, 20, 73]. Other techniques include analysis in the frequency domain, which also assumes a known source distribution [22]. Direct least-squares fitting of 2-D ring images from a single spectral line has been proposed, but is mainly aimed at calibrating and characterizing visible laser diodes [74]. Another alternative is data inversion [24, 75, 76], which can be effective in cases where the spectrum is unknown. Abbiss and Heeg measured spectra by varying the input angle of a tunable filter [75]. While such scanning methods are not suitable for pulsed, imaging LIBS applications, similar
mathematical principles were used in this case. The reconstruction method used to interpret the high-resolution spectrum captured by a hybrid interferometric/dispersive spectrometer takes into account the distribution of fringes observed in a 2-D image, and can be applied to spectra of a broadband source without presuming the shape of the input spectrum.

4.2 2-D instrument function

![Figure 4.1. Schematic diagram of experimental setup.](image)

The fringe pattern is an angular pattern, that depends on wavelength, arising from constructive and destructive interference [77, 78]. A broad and complex spectrum incident on the Fabry-Perot etalon may produce a transmission pattern that cannot be uniquely reconstructed. This is due to degeneracy inherent in the interference pattern produced by the etalon, which exhibits a characteristic periodicity and wavelength-angle coupling, whereby an identical phase shift can be produced by different combinations of wavelength and transmission angle. This degeneracy can be broken by coupling the etalon to a dispersive spectrometer, which provides
an additional angular dispersion, as described by Effenberger et al [26]. A diagram illustrating the approach to image sampling and dispersion is shown in Figure 4.1. The high-resolution spectral information is encoded on the axis parallel to the spectrometer slit (i.e., orthogonal to the dispersion plane of the spectrometer). The production of the interference ring pattern by the Fabry-Perot etalon can be described as

\[ B(\theta) = \int_{0}^{\infty} T(\theta, \lambda) A(\theta, \lambda) d\lambda, \quad (4.1) \]

where \( A(\theta, \lambda) \) is the light incident on the etalon and \( B(\theta) \) is the spectrally integrated spectrum of the transmitted light. The Fabry-Perot etalon transmission function is described by Equation (3.8).

In a typical Fabry-Perot optical arrangement, the transmission pattern is measured in the focal plane of a lens (far field). The fringe pattern measured in this way is comprised of concentric rings of light corresponding to the angularly and spectrally dependent interference maxima arising from propagation through the Fabry-Perot etalon. The maxima appear when the condition \( \cos (\theta) / \lambda = k\pi / (2\pi Dn) \) is met (where \( k \) is an integer). Degeneracy arising from the coupling of angle and wavelength can be broken by introduction of angular dispersion, which leads to the measurement of

\[ B(\theta, \lambda) = T(\theta, \lambda) A(\theta, \lambda). \quad (4.2) \]

Here, \( B(\theta, \lambda) \) represents the recorded 2-D interference pattern. The measurement of this pattern is typically limited by the available spectral resolution, which is dictated by the properties of the arrangement used to produce dispersion and the size of the detector pixels. At any wavelength \( \lambda_0 \), the quantity measured is

\[ B(\theta, \lambda)|_{\lambda=\lambda_0} = \int_{\lambda_0-\epsilon/2}^{\lambda_0+\epsilon/2} T(\theta, \lambda) A(\theta, \lambda) d\lambda, \quad (4.3) \]

where \( \epsilon \) is the spectral resolution at wavelength \( \lambda_0 \). It is assumed for the purpose of this analysis that the resolution in the angular direction (\( \theta \)) is sufficient to
accurately measure the shape of $B(\theta, \lambda)|_{\lambda=\lambda_0}$. It is further assumed that light incident on the etalon does not exhibit angular dependence of the spectrum, so that the angular dependence of $B(\theta, \lambda)$ arises solely from the nonuniform angular fringe profile and $T(\theta, \lambda) = B(\theta)A(\lambda)$. The light is incident on the etalon from the output of an optical fiber, and the Gaussian model [79, 80] chosen for the angular dependence of the fringe distribution is

$$B(\theta) = B_0 \exp \left( -\frac{(\theta - \theta_0)^2}{w^2} \right) + C,$$  \hspace{1cm} (4.4)

where $B_0$ is the Gaussian envelope, $\theta_0$ is the angle corresponding to the etalon axis, $C$ is a constant, and $w$ is the width of the distribution envelope. The envelope function (a smooth curve that outlines an oscillating signal) can be used to correct the measured Fabry-Perot pattern for its angular dependence by fitting it to the Gaussian envelope $B(\theta)$.

The Fabry-Perot ring pattern is formed by the etalon mapping light of different wavelengths to their corresponding angles. The processes of mapping an incoming beam of light can be calculated as a two dimensional linear transformation. A transformation $T$ is linear if for vectors $u$ and $v$,

$$T(u + v) = T(u) + T(v)$$  \hspace{1cm} (4.5)

and

$$T(ru) = rT(u),$$  \hspace{1cm} (4.6)

where $r$ is a real number. The transformation can be represented by a matrix operation

$$B_{\theta_j} = T_{\lambda_i, \theta_j} A_{\lambda_i},$$  \hspace{1cm} (4.7)

where $A_{\lambda_i}$ is an array of spectral counts as a function of wavelength and $B_{\theta_j}$ is a profile of Fabry-Perot fringes as a function of angular displacement from the
optical axis. $T_{\lambda_i,\theta_j}$ is the 2-D instrument function of the Fabry-Perot spectrometer, based on Equation (3.8): The left side of Equation (4.7) is a linear transformation because the variables of the instrument transmission matrix have known values. The transformation is a linear combination of the individual contributions to the interference pattern by light in a specified wavelength $\lambda$ range for a given angle $\theta$. Experimentally, $A_{\lambda_i}$ is the true emission distribution of the plasma, assuming broadening contributions from the auxiliary grating spectrometer are negligible. Equation (4.7) is applicable to any $n \times 1$ input spectral input array. The $n \times n$ transform matrix is defined for a range of $\theta$ and $\lambda$. The transform matrix $T_{\lambda_i,\theta_j}$ is built from the Airy function based on the known specifications ($n$, $r^2$, $D$) of the Fabry-Perot etalon.

![Figure 4.2](image_url)

**Figure 4.2.** The 2-D instrument function for the Fabry-Perot spectrometer for $-46 \text{ mrad} \leq \theta \leq 46 \text{ mrad}$ and $312.4 \text{ nm} \leq \lambda \leq 312.8 \text{ nm}$.

The model makes several basic assumptions. First, incoming light is treated as an infinite plane wave, when in actuality the incoming light has a finite angular divergence. Next, the quantities $r$, $D$, and $n$ are constant in the defined $\theta$ and $\lambda$ range. Lastly, the model does not take into account imperfections in the optics or
distortions in the wavefront after multiple reflections. The output vector $B_{\theta_j}$ is a profile of the interference pattern about the diameter of the cylindrically symmetric ring system after it has been imaged onto the entrance slit of a spectrograph and dispersed in the $x$-direction by a grating. The model does not account for the curvature of the 2-D ring pattern or the partial view of the ring pattern imposed by the finite slit width of the auxiliary spectrometer.

The entrance slit of the spectrometer is usually opened wider than for conventional use (up to several hundred micrometers wide) in order to obtain an image of the Fabry-Perot fringes. If the resolution of the grating is sufficiently high to separate the ring pattern of two lines of wavelengths differing by the sum of one free spectral range of the Fabry-Perot interferometer and the slit width, the ring patterns will appear offset on the final image. If the resolution is lower, then the rings will partially overlap. If the resolution is too low to separate the two images, the patterns will become superimposed.

![Figure 4.3. Example of Fabry-Perot spectrometer mapping spectral lines (left) to corresponding interference profiles (right) via the instrument function shown in Figure 4.2. The effects of spectral broadening on the interference pattern are shown for a delta function (black), and lines with a FWHM of 10 pm (red), and 30 pm (blue). The fringe pattern subtends only a few (~3) degrees.](image)

An illustration of the effects of peak broadening of the Fabry-Perot spectrum is shown in Figure 4.3. The broadened line profile is approximated by a Lorentzian, assuming that the line width is determined mostly by Stark broadening, with Doppler broadening being negligible [81, 82]. The calculation assumes that
broadening results in a symmetric line profile, although it is possible for asymmetric broadening to occur in LIBS emission [83]. The Lorentz function is given by

$$I(\lambda_i) = \frac{1}{\pi} \frac{(\Delta \lambda/2)}{(\lambda_i - \lambda_0)^2 + (\Delta \lambda/2)^2},$$

which is a function of $\lambda_i$, where $\lambda_0$ is the central wavelength, and $\Delta \lambda$ is the FWHM. The central wavelength for this example is $\lambda_0 = 312.57$ nm and the angular and spectral range is defined as $-46$ mrad $\leq \theta \leq 46$ mrad and $312.4$ nm $\leq \lambda \leq 312.8$ nm, respectively. The line shapes are shown on the left panel in Figure 4.3. The Fabry-Perot etalon in this example is characterized by $n = 1$ (air spaced), $r^2 = 0.95$ (reflectivity), and with $D = 0.44$ mm (end mirror spacing). The curves were calculated using 1024 points to adequately sample the instrument function. The broadening of the delta peak in Figure 4.3 is attributed solely to the Fabry-Perot instrument broadening.

### 4.3 Reconstruction of high-resolution spectra

When comparing different instruments and configurations for making LIBS measurements, tradeoffs between sensitivity, resolution, sampling frequency, and SNR should be considered. The accuracy of peak fitting analysis for reconstruction of high-resolution LIBS spectra from the Fabry-Perot fringes can be affected by the combination of instruments used for the measurement.

The procedure for reconstructing high-resolution spectra from Fabry-Perot measurements involves peak fitting procedures and comparison of the calculated Fabry-Perot transmission to experimental data in order to determine the best fit parameters. However, the Airy transmission function assumes that the transmitted light forms infinite plane waves and uniform interference patterns. In actual measurements, the line strength of the fringe profile decays at positions more distant from the center of the ring (optical axis) [79, 80, 84, 85]. Also, asymmetric
peaks may be observed because of optical distortions and discrete image sampling by pixels of the detector array.

Line strength of the fringes decreases at increasing angle from the central axis, and should be taken into account when conducting spectral analysis. One approach to mitigating asymmetry in the measured fringes is to use an alignment procedure prior to collecting data. The major drawback of this approach is that it requires numerous moving parts, since the distribution of light in the Fabry-Perot etalon is highly sensitive to the incident angle and relative position of the optical components of the system. The distribution of LIBS emission light is not uniform and alignment with a laser beam may not mitigate asymmetry of measured LIBS data.

This model of the measurement can be used for reconstructing the high-resolution features in the input spectrum directly from the measured pattern produced from the hybrid instrument, without making additional assumptions regarding the shape of the spectrum. In a real measurement, the discretization and normalization (to the best-fit envelope function $A(\theta)$) of the measured transmission pattern in the neighborhood of the wavelength $\lambda_0$ yields the vector described in Equation (4.7). Here, $T_{\theta,\lambda}$ is the transmission matrix constructed by discretization of Equation (3.8), and $A_{\lambda}$ is the vector representing the spectrum in the vicinity of the wavelength $\lambda_0$. The high-resolution spectrum can then be reconstructed as

$$A_{\lambda} = T_{\theta,\lambda}^{-1}B_{\theta},$$

which is, in practice, reduced to finding the least-squares solution to this inverse problem. Least-squares fits have been used to analyze the source spectrum transmitted by a Fabry-Perot interferometer [75, 86]. For the reconstruction of the source spectrum $A_{\lambda}$, the least-squares solution to the system is determined by
multiplying both sides of the equation by $T^{-1}_{\lambda_i, \theta_j}$.

\[
T^{-1}_{\lambda_i, \theta_j} B_{\theta_j} = \left( T^{-1}_{\lambda_i, \theta_j} T_{\lambda_i, \theta_j} \right) A_{\lambda_i}
\]

\[
T^{-1}_{\lambda_i, \theta_j} B_{\theta_j} = IA_{\lambda_i}
\]

\[
T^{-1}_{\lambda_i, \theta_j} B_{\theta_j} = A_{\lambda_i}
\]

where $I$ is the identity matrix. However, the inversion of $T_{\lambda_i, \theta_j}$ can be a challenge if it is ill-conditioned. By definition, an ill-conditioned matrix is a matrix with a very large condition number [87]. Conversely, a well-conditioned matrix has a condition number close to 1. The condition number of a matrix is a way of quantifying how well $B_{\theta_j} = T_{\lambda_i, \theta_j} A_{\lambda_i}$ can be approximated, and measures how sensitive the output of the function can vary for a small change in the input value. In other words, the condition number is a measure of how the accuracy of a solution of a system of linear equations is affected by small variations, such as noise, in experimentally measured data [25]. For extremely ill-conditioned matrices, the problem may not be possible to solve.

A system of equations can be approximated by least-squares by minimizing the residual error $E_r$,

\[
E_r = T_{\lambda_i, \theta_j} A_{\lambda_i} - B_{\theta_j}.
\]

(4.11)

The norm of $E_r$ satisfies

\[
\|E_r\| = \|T_{\lambda_i, \theta_j} A_{\lambda_i} - B_{\theta_j}\|.
\]

(4.12)

The least-squares estimate of the solution to $B_{\theta_j} = T_{\lambda_i, \theta_j} A_{\lambda_i}$ finds $A_{\lambda_i}$ such that it minimizes $\|E_r\|$, the norm of $E_r$. 
4.4 Implementation

The least-squares technique has been implemented using Wolfram Mathematica to solve a system of linear equations. The condition number of the matrix, defined as $\|m\|$, is approximated by the function `LinearAlgebra`MatrixConditionNumber[m]` [88]. The function `LeastSquares[m, b]` solves the linear least equation $m.x = b$ for vector $x$.

The least-squares solution can also be calculated by finding the pseudoinverse of the 2-D matrix function of the Fabry-Perot spectrometer. `LeastSquares[m, b]` can also be obtained by calculating `PseudoInverse[m], b`. Another equivalent expression is `ArgMin[Norm[m.x - b], x]` [89]. The estimation of the input $x$ is sensitive to the numerical tolerance, which determines the numerical roundoff error of $x$. 
Experimental setup

5.1 Analysis of system components

5.1.1 Overview

A typical benchtop LIBS system is composed of a pulsed laser, guiding and focusing optics, a sample holder and collection optics, a spectrometer, and an imaging detector (e.g., CCD, ICCD). Data processing and timing is computer controlled [90]. When considering the design of a field-deployable instrument, instrument size, weight, cost, performance, and robustness need to be taken into account.

5.1.2 High-resolution instruments

Table 5.1 compares the spectrometers that have successfully measured isotopes of nuclear materials. The DEMON and EMU-65 were used by Cremers et al. [30] and the 2 m Model 2062 spectrometer was used by Smith et al. [28]. These spectrometers are coupled to ICCD detectors.

The experimental setup of the high-resolution Fabry-Perot spectrometer system used by Effenberger and Scott are described in Table 5.2. High-resolution spectrometers such as advanced echelle systems or long focal length Czerny-Turner
spectrometers tend to be costly and large [43]. Coupling a Fabry-Perot etalon to a medium-dispersion spectrometer and utilizing an ICCD detector with a 2-D array provides an inexpensive alternative to a high-resolution, compact spectrometer for LIBS.

Table 5.2. Specifications of the Fabry-Perot etalon and spectrometer used for high-resolution LIBS measurements by Effenberger and Scott [43]. Approximate costs are listed.

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<th></th>
<th>SpectraPro (PI Acton)</th>
<th>Custom design (SLS Optics)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Czerny-Turner</td>
<td>Etalon</td>
</tr>
<tr>
<td>Res. power ($\frac{A}{\Delta \lambda}$)</td>
<td>8,700</td>
<td>57,000 (313.1-nm)</td>
</tr>
<tr>
<td>Weight (kg)</td>
<td>18</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>Size (cm)</td>
<td>53.4 x 28 x 20.3</td>
<td>3.6 (diam.) x 3.5</td>
</tr>
<tr>
<td>Cost ($)</td>
<td>15K</td>
<td>3K</td>
</tr>
</tbody>
</table>

Isotope ratios are challenging to determine because of plasma properties and instrument limitations. Analysis of uranium requires instruments of high spectral resolution and carefully selected experimental parameters (e.g., delay and
acquisition time, ambient conditions). Previous measurements of the isotopic shift of nuclear materials have been carried out in low gas pressure because LIBS conducted in ambient air exhibits greater Stark broadening [27, 28, 91]. The ideal plasma conditions for detection of isotopes are prolonged emission lifetime with high intensity and narrow line widths [92, 93]. Therefore, the proper delay and gate time should be selected for the measurement. However, the isotope shift of uranium is small and mathematical deconvolution via multi-component analysis and partial least squares techniques are often used to reconstruct isotope ratios from complex line shapes and partially resolved spectral peaks [29, 94]. The accuracy of mathematical reconstruction of isotope ratios depends on the resolution of the instrument [95].

5.2 Spectral sampling

The resolution of a detector depends on the number and size of the pixels relative to the image or spectrum in the focal plane. Sampling is performed by the pixels of the detector array, and can influence the accuracy of spectral fitting. A measured image is therefore a discrete signal, sampled from a real, continuous signal in the focal plane of the detector. In order to ensure faithful reproduction of the input image, the Nyquist criterion should be fulfilled. The Nyquist sampling theorem states that the sampling frequency should be twice the smallest feature, or highest frequency, in the image or spectrum. The sampling frequency is critical to adequate representation of the image or spectrum [96]. The accuracy of a fit or signal processing approach increases with greater sampling, or number of pixels on the feature of interest. Three pixels are typically necessary to cover a spectral or image feature to faithfully reproduce it. For certain cases only one pixel may suffice, such as when an object image is smaller than the size of a pixel [97].

For a detector coupled to a spectrometer, the spectral sampling interval of
the detector is equal to the spacing between pixels in the measured spectrum. The discrete sampling interval is often smaller than the spectral resolution of the instrument, which is defined by the smallest feature that can be resolved. For a conventional spectrometer coupled to a detector array, the bandpass is the width of the spectral response of the spectrometer. The lower limit of the bandpass is determined by the detector size and the optical geometry of the spectral system. Nyquist sampling requirements are met when the bandpass is spread across two pixels. The bandpass may be reduced by decreasing the slit width until the spectral resolution is pixel-size limited. This condition is known as critical sampling [98]. In a setup that utilizes a Fabry-Perot etalon, the sampling of the image is not limited by the slit width. Efficient sampling of the ring profile is, instead, dependent on the pixel size of the detector array, the finesse of the etalon, and the ring density in the focused image.

The spatial resolution of the detector array of the ICCD is important for adequate sampling of an image or spectrum. The sampling frequency and spatial resolution increase as pixel size decreases for a given spectral window. Conversely, the larger the pixel size the lower the resolution, but the higher dynamic range and hence a higher signal-to-noise ratio [99].

The finesse of the Fabry-Perot etalon limits the resolution attainable by the device. The width of transmission peaks decreases for high-finesse etalons, resulting in higher resolution. However, lower transmission occurs at positions of high reflectivity of the partially transmitting etalon mirrors. Therefore, there is a direct trade-off between sensitivity and resolution of the Fabry-Perot etalon.

The density of interference fringes of the ring pattern is dependent on the focal length of the fringe focusing lens. The spread of interference peaks incident on the detector array determines the sampling rate of each peak. For dense ring patterns, the signal-to-background is high because a larger fraction of the collected light is imaged. However, each spectral feature is spread across fewer pixels. When a
longer focal length lens is used, each spectral feature is more highly sampled but exhibits lower intensity.

The transmission function maps spectral areas to corresponding spatial areas, so each wavelength bin is mapped to the spatial (angular) domain. For large angles, the density of the circular fringes, described by the Airy shape function, increases as shown in Figure 5.1. In experimental applications, the bright fringes at larger angles begin to overlap and become difficult to resolve because the phase shift increases more rapidly while lateral spatial resolution decreases. In spectroscopic applications in which a Fabry-Perot etalon is used, the experimental parameters should be adjusted to image the desired field of view.

![Figure 5.1. Transmission intensity fringe patterns, predicted by the Airy shape function, with $0 < \theta < 0.058$ rad (left) and $0 < \theta < 0.086$ rad (right). Fringes shown have parameters $n = 1$, $D = 0.44$ mm, $r = 0.95$, $\lambda = 313.01$ nm. The density of fringes formed in the focal plane of the focusing lens in a Fabry-Perot etalon setup decreases with focal length of the lens used.](image)

### 5.3 Experimental setup

At the center of any LIBS experiment is the selection and setup of its apparatus, which usually includes the laser, sample introduction system, timing system,
spectrometer, and detector.

A stainless steel vacuum chamber was designed by Ko et al. [18], and fabricated with five viewports and supplementary vacuum, electric, and gas feedthroughs. In addition to the windows placed to allow beam access perpendicular and parallel to sample surface, the chamber has also been fitted with viewports at 45° with respect to sample surface. Window ports were machined out of PVC material to house optical windows that are easily interchangeable, such that windows specifically coated for different ranges of wavelengths can be used. The vacuum performance of the vacuum chamber was tested, with the chamber initially evacuated to $10^{-4}$ mbar using a vacuum system consisting of a roughing and turbo pump. The chamber was subsequently sealed off from the pump using a mechanical valve. Initially the pressure increases rapidly to a steady state at $10^{-2}$ mbar. Then, the pressure increases at a slow rate of 0.01 mbar per hour. The lowest pressure that could be achieved by pumping the chamber over an extended period was $10^{-5}$ mbar.

Samples are mounted on scanning electron microscopy holder stubs and affixed to a three-axis translation stage. The stage (Thorlabs vacuum compatible PT3) is translated by three vacuum compatible picomotor actuators (Newport New Focus 8302-V), with < 0.30 nm incremental motion resolution and a range of 2.5 cm. The holders can be readily removed and transferred for any subsequent post-LIBS characterization.

The light emitted from the plasma is collected and collimated by a 5-cm focal length lens mounted off-axis to the laser beam path. A second lens focuses the collimated light into an optical fiber. The opposite side of the optical fiber is directed to the Fabry-Perot etalon. A holder was built to couple the etalon to the spectrometer. In measurements where the etalon was not used, the fiber was directly routed to couple to the entrance slit of the spectrometer.
Figure 5.2. Oscilloscope trace showing the external trigger (blue), ICCD gate (black), and photodiode trace (red). ICCD delay is adjusted until the ICCD gate opening corresponds to the arrival of the laser pulse at the sample \( t = 0 \).

5.3.1 Experimental timing

Accurate control of timing is imperative in LIBS studies to properly capture the plasma emission at various stages of plasma evolution. The timing for data collection is defined relative to a reference time \( t = 0 \), which corresponds to the laser pulse and the rising of the plasma emission intensity. Assuming that the time between laser-pulse arrival and plasma formation is negligible \(< 1\text{ ns}\), the ICCD gate signal can be set relative to the reference time by adjusting the delay time until it is at \( t = 0 \). This was accomplished by placing a photodiode (Thorlabs DET-10A) in front of the sample chamber to detect the laser pulse. An oscilloscope (LeCroy) was used to check the delay between the trigger signal from the laser and the arrival of the laser pulse. The proper delay was input to establish \( t = 0 \) for LIBS experiments. The oscilloscope showing the trace at \( t = 0 \) is shown in Figure 5.2.

For conventional LIBS applications, timing control is implemented using a delay generator (Stanford Research Systems DG 645) that is triggered by the Q-switch signal from the laser at a proper time delay. The delay generator triggers a mechanical shutter (Uniblitz VS-25), ICCD, and the picomotor actuators. The
shutter can operate at 10 Hz during continuous operation with a minimum opening window time of 10 ms. The shutter is opened after the delay generator receives a trigger signal to select a single laser pulse. The ICCD camera records the emitted light at a selected time after the arrival of the trigger pulse. Subsequently, the actuators translate the sample after the spectrum is collected in order to expose a fresh, previously unablated region on the sample surface on the next laser shot. The experimental timing configuration is depicted in Figure 5.3.

In the timing setup for the hybrid configuration, the laser triggers the ICCD at a 10 Hz repetition rate, as depicted in Figure 5.4. To improve the signal-to-noise, the ICCD Integrate on chip (IOC) function was used in experiments. In this mode the light passes through the intensifier while it is switched on. The CCD chip collects light continuously during the exposure while the intensifier gates on and off. Charge is built up on the sensor and read out at once at the end of the exposure. The noise from the detector is generated only from a single readout. In
accumulate mode, the CCD is read a number of times and accumulated, summing the noise in each readout.

5.4 Alignment of Fabry-Perot etalon

The mathematical analysis presented in Chapter 4 applies to symmetric, centered Fabry-Perot etalon fringes incident on the entrance slit of the spectrometer. If the optics of the etalon system are displaced from the optical axis, which is cylindrically symmetric, off-axis or asymmetric fringes may result. To ensure that angle of the Fabry-Perot output subtended by the spectrometer entrance is on-axis, the etalon is mounted in such a way that its position is adjustable with six degrees of freedom.

A LabVIEW program was written to analyze the image acquired by the ICCD. Once the fringes are visible on the detector, the program is able to select a portion

Figure 5.4. Schematic diagram depicting timing setup for LIBS measurements using the hybrid spectrometer.
of the image from the camera to integrate across the horizontal axis to view the profile of the interferogram in real time, as shown in Figure 5.5(b). The alignment procedure is performed prior to data collection.

![Figure 5.5. LabVIEW beam alignment program user interface. The calibration source is an Hg(Ar) lamp. The image acquired from the camera (a) is converted to a 1-D interferogram (b) in real time. Beam alignment is performed by adjusting the position of the etalon until one half of the spectrum is superimposed with the other (c) and the difference between the two (d) is minimized.](image-url)
Experimental results and discussion

6.1 Analysis of mercury lines

Combining the benefits of 2-D algorithms with the speed necessary for rapid and high-resolution fringe measurement, the mathematical analysis technique developed was experimentally verified with an Fabry-Perot fringe imaging system. The hybrid spectrometer, when used in conjunction with the reconstruction technique discussed here, represents an effective tool for measuring the high-resolution spectrum with accurate peak intensity ratios. Rapid, high-resolution spectral reconstruction capability from this type of measurement is ideal in certain applications of LIBS. The resolution of the hybrid interferometric/dispersive approach is at least an order of magnitude greater than the resolution of the grating spectrometer alone. This instrument can achieve the desired high resolution for measurement of the atomic isotope shift of uranium, while reducing the size and cost of the instrument by approximately an order of magnitude.

The reconstruction method was applied to data collected from a hybrid spectrometer that used a 550 mm focal length imaging spectrometer (Horiba Jobin Yvon) equipped with a 1800 mm$^{-1}$ grating and a 1024×1024 pixel array iStar ICCD (Andor) composed of 13 µm pixels. Coupled to the entrance of the
spectrometer was a Fabry-Perot etalon (SLS Optics). Light was transmitted to the etalon by a multimode 400 µm core diameter optical fiber (Ocean Optics). Fiber-optic connector, etalon, and lens were affixed in a cage setup, with multi-axis adjustments to enable accurate alignment of the circular transmission pattern to the spectrometer slit. A 25 mm diameter lens with a focal length of 100 mm was used to focus the output of the etalon onto the entrance slit of the spectrometer. The light source used was a mercury-argon calibration pen lamp (Oriel).

The Fabry-Perot etalon was coupled to the entrance slit of the spectrometer to produce fringes, as shown in Figure 6.1(a). The section of the spectrum corresponding to the Hg I 313.1555/Hg I 313.1844 nm doublet was summed along the horizontal axis to obtain the 1-D profile of the transmitted intensity, shown in Figure 6.1(b). The symmetric fringes were summed about center of the pattern. A Gaussian envelope function was fit to the fringes exhibiting a characteristic double-peaked shape to obtain the $A(\theta)$ correction, as shown in Figure 6.1(c). The normalized transmitted intensity pattern is shown in Figure 6.1(d).

It is necessary to calibrate the angular axis before formulating the instrument function. This calibration was performed using the neighboring Hg I 312.5674 nm line (Figure 6.1(a)). The angular position of highest intensity (peak) in the fringe profile was used to perform the calibration in Figure 6.2. Since the paraxial approximation is valid, the calibration can be described by a linear function, also shown in Figure 6.2. The region of the fringes selected for this fit did not include the area near the optical axis or the outermost fringes, which may exhibit distortions due to their low intensity and possible optical aberrations.

Next, the instrument function for the 313 nm doublet was determined. The ranges of $\theta$ and $\lambda$ used to construct the instrument function were $20 \text{ mrad} < \theta < 32 \text{ mrad}$ and $313.106 \text{ nm} < \lambda < 313.234 \text{ nm}$, respectively. The etalon had air-spaced ($n = 1$) mirrors separated by a distance of $D = 0.44 \text{ mm}$. The etalon reflectivity ($R = 0.73$) was determined by fitting the measured intensity profile to the known
Figure 6.1. (a) Measured pattern corresponding to the (I) 312.5674 nm line and (II) 313.1555/(III) 313.1844 nm doublet; (b) 1-D integrated profile of doublet; (c) intensity envelope function for (II) 313.155 nm (solid black circles – experimental data; dashed line – fit to Equation (4.4)); (d) normalized 1-D profile [100].

Fabry-Perot etalon transmission function, Equation (3.8), as shown in Figure 6.2.

Interpolation between points and increased sampling of the experimental spectrum was performed prior to reconstruction of the source spectrum, $A_\lambda$. The least-squares solution to the system of linear equations associated with Equation (4.9) could have been used to reconstruct $A_\lambda$. However, Equation (4.9) is an example of a problem where $T_{\theta,\lambda}$ is an ill-conditioned matrix [25]. Hence, the pseudoinverse $T_{\theta,\lambda}^+$ of the matrix was used to calculate a least-squares solution to the system of equations using the pseudoinverse in (4.9). The pseudoinverse solution was implemented in Mathematica (Wolfram Research) using the function `pseudoinverse`. Because of the ill-condition of the matrix $T_{\theta,\lambda}$, it was necessary to specify the tolerance parameter. The singular values matrix are the non-negative square roots of the eigenvalues of $T_{\theta,\lambda}^* T_{\theta,\lambda}$, where $T_{\theta,\lambda}^*$ is the conjugated transposed matrix.
Singularity values smaller than the product of the tolerance and the largest singular value of $T_{\theta, \lambda}$ are omitted [101]. In practice, the choice of tolerance controls the influence of smaller singular values in the composite error of the reconstruction, and is a tradeoff between reducing round-off error at the expense of a larger residual. A tolerance of 0.1 was used throughout the analysis to yield the optimal approximation to the solution.

Minimization of the residual error of the reconstruction was the next step. The widths of mercury lines from a low-pressure discharge calibration lamp are approximately 1 pm [30]. The width of the reconstructed spectrum is dictated primarily by the reflectivity $R$. Because the widths are narrow compared to the instrument function, an accurate reconstruction assuming this experimentally determined reflectivity was not possible. By assuming a broader source spectrum, it was possible to minimize residual error in the spectral reconstruction. A reflectivity value of $R_\alpha = \alpha R$, where $\alpha$ is a multiplicative constant of $R$ that minimizes the residual...
error, $\| B_\theta - T_{\lambda, \theta} A_\lambda \|$ was assumed. An optimal value $\alpha = 1.16$, obtained by scanning a range of values $1.00 < \alpha < 1.30$, was used to minimize the residual error of the reconstruction.

The spectrum of mercury measured using the grating spectrometer is shown in Figure 6.3(a) for comparison. The resolution ($\sim 70$ pm) is not sufficient for resolving the 313 nm doublet. The final reconstruction results from the hybrid spectrometer is shown in Figure 6.3(b) and summarized in Table 6.1. The resolution is $\sim 8$ pm, which exceeds the resolution of the grating spectrometer by one order of magnitude. In comparison, Effenberger et al. [43] estimated the resolution to be $\sim 11$ pm from the measured peak separation.

Correcting for the angular drop in intensity of the measured Fabry-Perot pattern was critical for peak ratio determination; the reconstructed peaks of non-normalized data yielded a ratio of 0.629, which is lower due to the decreasing intensity as a function of distance from the interferogram center. Validation of the reconstructed spectrum was performed by comparing the results with those acquired with a high-resolution echelle spectrometer (DEMON, Lasertechnik Berlin) using the same mercury-argon lamp. The DEMON results are also provided in Figure 6.3 and Table 6.1, along with literature values [102].

Averages reported in Table 6.1 are based on 10, 5, and 20 spectra for sources 1, 2, and 3, respectively. The reconstructed peak wavelengths are 313.156 nm and 313.185 nm for the mercury doublet, and agree well with actual values. While the resolution is not as high for the hybrid spectrometer, the spectra are similar (Figure 6.1) and give a very similar ratio accuracy (Table 6.1).

To further explore the usefulness of this spectral reconstruction method, it was applied to the analysis of LIBS data from the mineral cinnabar (mercury sulfide) acquired with a different hybrid spectrometer [43]. In this case, plasma was generated by 1064 nm laser pulses at 25 mJ per pulse, and the emission light was coupled into a fiber optic connected to a Fabry-Perot attached to a 500 mm
Figure 6.3. (a) The (I) 312.5674 nm line and (II) 313.1555/(III) 313.1844 nm doublet measured with the grating spectrometer alone; the doublet (II+III) is not resolved. (b) The spectrum of the (II) 313.1555/(III) 313.1844 nm doublet (black, dotted) reconstructed by the hybrid spectrometer and DEMON measurement (blue, solid). LIBS of mercury sulfide reconstructed by the hybrid spectrometer measurement is also shown (red, solid) [100].

Grating spectrometer with a 512×512, 24 µm/pixels detector array. The spectrum was collected from the accumulation of 600 laser pulses at a rate of 10 Hz and under 10 Torr He atmosphere, which is the optimum pressure for the mercury 313 nm doublet [43]. The reconstructed doublet, shown in Figure 6.3(b), exhibits a ratio of 0.682 and is in good agreement with values reported in Table 6.1. Peak
Table 6.1. Peak ratios of the 313 nm doublet of a mercury-argon calibration lamp measured by different methods. The same lamp is measured by method 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>Ratio</th>
<th>Uncert.(%)</th>
<th>$\lambda/\Delta\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hybrid spectrometer</td>
<td>0.682</td>
<td>1.8</td>
<td>$\sim37{,}000$</td>
</tr>
<tr>
<td>2. DEMON</td>
<td>0.681</td>
<td>2.4</td>
<td>$\sim75{,}000$</td>
</tr>
<tr>
<td>3. Ref. [102]</td>
<td>0.687</td>
<td>7.2</td>
<td>N/A</td>
</tr>
</tbody>
</table>

broadening in the LIBS spectrum is due to plasma dynamics [103].

6.2 Etalon/lens coupling for uranium measurements

Two broadband coated Fabry-Perot etalons were available to use with the optical setup in our experiment for the uranium lines of interest. A narrowband Fabry-Perot etalon coated specifically for the spectral region near the mercury lines of interest had been used for the mercury line measurements. The wavelength coverage of both broadband etalons cover the spectral region where uranium lines of interest appear. The two broadband designs and their respective descriptions are listed in Table 6.2. With a mercury-argon calibration lamp and three commercially available lenses (focal lengths 75 mm, 100 mm, 125 mm and 150 mm) for fringe-focusing, the performance of the two etalons were compared. The mercury 435.84 nm line was used for the measurements.

The fringes of the mercury 435.84 nm line generated with the #A40a etalon using two different focal length lenses are in Figure 6.4. Figure 6.5 shows the fringes, from the same mercury lamp line, when #A510 etalon is used. The main differences between the two etalons are the end mirror separation $D$ and the mirror
Figure 6.4. Fabry-Perot etalon Design #A40a measurement of mercury 435.84 nm line using (a) 75 mm focal length lens and (b) 100 mm focal length lens. The corresponding fringe pattern, imaged by the detector, is shown at the bottom of each spectrum.

Table 6.2. Description of Fabry-Perot etalons from SLS Optics.

<table>
<thead>
<tr>
<th></th>
<th>Design #A40a</th>
<th>Design #A510</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coating</td>
<td>Broadband</td>
<td>Broadband</td>
</tr>
<tr>
<td>λ coverage (nm)</td>
<td>424–662</td>
<td>400–600</td>
</tr>
<tr>
<td>D (mm)</td>
<td>0.44</td>
<td>1.25</td>
</tr>
</tbody>
</table>

coating (which determines the etalon reflectivity). Because the angles of different fringe orders depends on \( D \) and \( R \), different focal length lenses were needed to
Figure 6.5. Fabry-Perot etalon Design #A510 measurement of mercury 435.84 nm line using (a) 125 mm focal length lens and (b) 150 mm focal length lens. The corresponding fringes, imaged by the detector, is shown at the bottom of each spectrum.

focus the desired amount of fringes onto the imaging detector. For example, Figures 6.5(b) and 6.6 show results from the same focal length lens coupled with the two different Fabry-Perot etalons.

Standard focal length fringe focusing lenses were selected for their commercial availability. Shorter focal length lenses bring a larger number of higher order fringes into the field of view of the detector (proportional to $1/f$, where $f$ is the focal length of the fringe focusing lens), because the fringes are focused at infinity. When a bright fringe appears at the center of the fringes, the diameter of the first
constructive interference ring from the center (optical axis) can be estimated as

\[ D_{ring} = 2f \sqrt[2]{\frac{\lambda}{D}}. \]  

(6.1)

This approximation applies to etalon \#A510, and is convenient when considering the optical setup. After comparing the \#A40a and \#A510 designs, the \#A510 was selected for its higher resolution and flatter baseline, as seen in Figure 6.5. The 150 mm focal length lens was chosen to be paired with the etalon because it resulted in a sufficient number of fringes in the field of view of the detector with ample spacing between fringes to reduce the possibility of overlapping orders when several different spectral lines are imaged.

6.3 Analysis of uranium lines

6.3.1 Samples

The samples used in our experiment were a 4.61 mm × 8.37 mm × 0.26 mm natural uranium foil (0.7% of $^{235}$U) and a 74 mm × 74 mm × 0.11 mm uranium foil highly...
enriched in $^{235}$U to 93%. Both samples were provided by the Penn State University’s Breazeale Nuclear Reactor. The natural uranium foil was mounted using double-sided carbon tape on an Al SEM stub. A separate Al holder was machined for the purpose of housing the bare highly-enriched uranium foil for safe handling and transport. Because the foils were legacy material from storage, gamma ray analysis was performed for further characterization. An HPGe (Canberra) detector acquired the gamma spectra. Enrichment of the foils obtained using Multi-Group Analysis for Uranium software (MGAU version 4.2) were 0.7% enrichment for the natural uranium foil and 96% for highly-enriched uranium. A detailed summary of the measurement is presented in Appendix C.

6.3.2 Temporal evolution

The samples were placed in a sealed experimental chamber and mounted to a sample holder at normal incidence to the laser beam. 10 ns laser pulses at a wavelength of 1064 nm were generated by a Nd:YAG laser (Spectra Physics). The laser pulses were focused onto the sample through a optical window using a 300 mm focal length lens. The emission from the plasma was collected and collimated by a 5 cm focal length lens mounted off-axis to the laser beam path. A second lens focused the collimated light into a 400 μm core diameter optical fiber which transmitted the light to the entrance slit (13 μm width) of the spectrometer. The detection system used composed of a 550 mm focal length imaging spectrometer (Horiba Jobin Yvon), 1800 mm$^{-1}$ grating and a 1024×1024 pixel array iStar ICCD (Andor), with 13 μm pixel size.

In order to determine the optimal delay time for isotopic measurements of U, the temporal evolution of the U II 424.437 nm line was studied. The uranium U II 424.437 nm line intensity, the associated continuum background, and the resulting signal-to-background ratio as a function of ICCD delay time are shown in Figures 6.7, 6.8, and 6.9, respectively. The plasma was generated in ambient
atmosphere using 30 mJ laser pulses. Spectra were collected with an ICCD gate width of 1 µs at varying delays in 1 µs increments. Each spectrum is the average of 5 repeated measurements, with contributions from detector noise removed prior to analysis. The sample was translated between each measurement, and cleaning shots were made prior to each measurement to remove the oxidized uranium surface [18].

**Figure 6.7.** Spectral line intensity of the U II 424.437 nm lines of natural uranium and highly-enriched uranium as a function of ICCD delay time. Error bars represent one standard deviation from the mean.

The line intensities and background continuum level were normalized to the intensity measured at delay time $t = 0$ for the purpose of comparison between the two samples. The continuum level was estimated using a low-pass filter. Generally, in Figures 6.7 and 6.8 the line intensity and continuum emission diminishes rapidly as a function of delay time until 5 µs is reached. The line intensity and continuum levels continue to decrease, although less rapidly, after 5 µs. The error bars and differences in plasma evolution trends is attributed to the inhomogeneity of the samples. The signal-to-background ratio was obtained by dividing the uranium peak intensity by the background continuum level. The plot of signal-to-background ratio as a function of delay time is shown in Figure 6.9. Although
Figure 6.8. Intensity of the continuum background levels as a function of ICCD delay time. Error bars represent one standard deviation from the mean.

The signal-to-background increases as a function of delay time, continuum emission was significantly reduced after 5 µs. Therefore, a delay time of 5 µs was chosen to maximize collected light and signal-to-background ratio.

Figure 6.9. Signal-to-background of the U II line as a function of ICCD delay time.

Figure 6.10 shows the spectra of natural and highly-enriched uranium, in the vicinity of the 424.437 nm line, measured using the 0.55 m Czerny-Turner spectrometer with an entrance slit width of 13 µm. Spectra were collected with an
ICCD gate width of 1 µs at a delay of 5 µs. The resolution of the 0.55 m Czerny-Turner spectrometer used in this measurement is not sufficient for resolving the isotope shift of U.

![Figure 6.10. LIBS spectra from natural uranium (gray line) and highly-enriched uranium (black line) foils measured using a 0.55-m Czerny-Turner spectrometer. The gray dashed lines indicate the positions of the of $^{238}$U 424.167 nm (I), 424.437 nm (II) and 424.626 nm (III) lines. Spectra were normalized to facilitate comparison.](image)

### 6.3.3 Hybrid interferometric/dispersive measurement

A 400 µm core diameter optical fiber (Ocean Optics) transmitted emission light to the broadband etalon (custom built by SLS Optics). The Fabry-Perot etalon was aligned to the entrance slit (500 µm width) of the spectrometer. A 25 mm diameter lens with a focal length of 150 mm was used to focus the light transmitted by the etalon onto the entrance slit of the spectrometer. Instrument alignment and spectral calibration was performed using an mercury-argon pen lamp (Oriel).

Because of the lower throughput of the high-resolution LIBS method using the hybrid spectrometer, each spectrum was collected from 600 laser shots (1 min exposure at a 10 Hz pulse rate). Because of the high repetition rate, the sample
was not translated between each pulse during the 1 min exposure. The gate time was set to 10 µs with 5 µs delay, and ICCD gain was set to 97.6% of the maximum gain.

Figure 6.11. (a) Measured pattern at the wavelength of 435.84 nm; (b) calibration of the angular (θ) axis using the location of three constructive interference peaks (black markers) and linear fit (dashed line); (c) best fit (dashed line) of the measured interference peaks by Equation (3.8) yields the reflectivity of the etalon (R = 0.77). Experimentally measured points are shown as black markers.

The hybrid spectrometer was aligned using the 435.84 nm line of an mercury-argon calibration lamp because of its proximity to the uranium lines of interest. The angular (θ) axis of the 435.84 nm fringes was calibrated by a linear fit, as shown in Figure 6.11(b). In Figure 6.11(c), etalon reflectivity was determined to be \( R = 0.77 \) by fitting the measured intensity profile of the mercury 435.84 nm line from a lamp to the Fabry-Perot etalon transmission function, corresponding
to a resolution of 6 pm at 424.437 nm. The intensity profile was obtained by summing along the horizontal (wavelength) axis of the image. Only half the fringes were analyzed due to cylindrical symmetry of the interference rings. The angular dependence of the intensity distribution (beam profile) is taken into account by convolving the fitting function with a Gaussian function. Figure 6.11(a) represents an accumulation of 10 spectra, with 1 s exposure each (10 shots), at 24.4% of the maximum detector gain.

**Figure 6.12.** Fringes measured with (a) natural uranium and (b) highly-enriched uranium sample in the vicinity of 424 nm. The first-order fringes of the $^{238}$U 424.167 nm (I), 424.437 nm (II) and 424.626 nm (III) lines are indicated in (a); in (b) the isotopically shifted (IS) $^{235}$U 424.173 nm (I$_{IS}$), 424.412 nm (II$_{IS}$) and 424.676 nm (III$_{IS}$) peaks are marked. Contrast and brightness in the images have been adjusted for clarity.

Performance of a conventional and hybrid spectrometer are compared to
understand the tradeoffs between sensitivity and resolution for measuring the $^{235}\text{U}/^{238}\text{U}$ isotope shift. Figure 6.10 shows the standard LIBS spectra comparing natural and highly-enriched uranium in the vicinity of the $\text{U II} 424.437$ nm isotope shift. The resolution of the 0.55 m Czerny-Turner spectrometer used in this measurement (70 pm) was obviously not sufficient for distinguishing between $^{235}\text{U}$ and $^{238}\text{U}$ lines.

**Table 6.3.** Uranium spectral lines studied in this experiment, their isotope shifts, atomic state (neutral I, singly ionized II).

<table>
<thead>
<tr>
<th>$^{238}\text{U}$ wavelength (nm)</th>
<th>Isotope shift (pm)</th>
<th>Atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>424.167</td>
<td>-6</td>
<td>II</td>
</tr>
<tr>
<td>414.437</td>
<td>25</td>
<td>II</td>
</tr>
<tr>
<td>424.626</td>
<td>5</td>
<td>I</td>
</tr>
</tbody>
</table>

The isotopically resolved measurement of uranium using the hybrid interferometric/dispersive spectrometer is shown in Figure 6.12. The profile of the fringes comparing natural and highly-enriched uranium are shown in Figure 6.13. Calibration of the angular ($\theta$) axis was based on the interference peaks of the $^{238}\text{U}$ lines. When a portion of the uranium 424.167 nm and 424.437 nm fringes was integrated, the isotope shift of the lines was distinguishable (Figure 6.13). Even without application of further mathematical functions, the isotope shifts of the 424.167 nm and 424.437 nm lines were easily measured to be $-6$ pm and $25$ pm, respectively, which agrees with previously observed values [30]. The 5 pm isotope shift of the $\text{U I} 424.626$ nm line was not studied due to partial overlap of the 424.626 nm and 424.412 nm fringes.

To further validate the resolution in measurement of the isotope shifts, experimental data were interpolated and resampled to improve the sampling rate for reconstruction via the inversion method. A low-pass filtering of the experimental data was also applied prior to reconstruction of the source spectrum to reduce
Figure 6.13. Integrated profile of the natural uranium (gray line) and highly-enriched uranium (black line) fringes. The peaks are labeled following the convention set in Figure 6.12. Peaks are normalized to show differences between natural and highly-enriched uranium. The 424.626 nm (III) line and isotope shift are not included in the analysis due to the overlap of the 424.412 nm (II_{IS}) and 424.676 nm (III_{IS}) interference lines.

random spectral noise. The isotopically shifted spectral lines, reconstructed using the inversion method, are shown in Figure 6.14. A tolerance of 0.3 was used to minimize error in the reconstruction. In order to generate the fringe profile of the 424.167 nm and its isotope shift, the 2-D image was summed along the x-axis in such a way that isolated the patterns from the two lines (spectrum not shown). The ranges of $\theta$ and $\lambda$ used to define the instrument function $T^{-1}_{\theta,\lambda}$ for reconstructing the 424.167 nm line in Figure 6.14(a) were $16 \text{ mrad} < \theta < 19 \text{ mrad}$ and $424.137 \text{ nm} < \lambda < 424.197 \text{ nm}$. For the same figure, $15 \text{ mrad} < \theta < 18 \text{ mrad}$ and $424.143 \text{ nm} < \lambda < 424.203 \text{ nm}$ were used to define $T^{-1}_{\theta,\lambda}$ for the 424.173 nm line. The 424.437 nm line and its isotope shift were reconstructed from a fringe profile obtained by summing along a portion of rings that included both the 424.167 nm and 424.437 nm interference rings. This could not be avoided due to the overlap of the fringes. For reconstructing the 424.437 nm line, $22 \text{ mrad} < \theta < 23.5 \text{ mrad}$ and
424.362 nm < λ < 424.462 nm. For the 424.412 nm line, 19 mrad < θ < 20.5 mrad and 424.387 nm < λ < 424.48 nm were used to define $T_{θ,λ}^{-1}$. Each line was reconstructed separately to avoid interference from adjacent spectral lines. Spectral line widths of 10 pm were measured at 424.437 nm and the 25 pm isotope shift was well resolved, while the −6 pm shift of the 424.167 nm line was partly discernible.

**Figure 6.14.** Reconstructed Fabry-Perot LIBS emission spectra of natural uranium (gray line) and highly-enriched uranium (black line) produced using the inversion method. (a) $^{238}\text{U}$ 424.167 nm (I) and $^{235}\text{U}$ 424.173 nm (IIS) lines (−6 pm shift); (b) $^{235}\text{U}$ 424.412 nm (IIIS) and $^{238}\text{U}$ 424.437 nm (II) lines (25 pm shift). Reconstructed spectra were normalized for comparison.
Chapter 7

Conclusions

7.1 Discussion

The instrument and spectral reconstruction approach for a hybrid interferometric/dispersive spectrometer demonstrates that simple, low-cost instruments with high resolution and accurate relative peak intensities can be realized. Accurate wavelength and ratio determination of mercury lines using this instrument has been presented, where the accuracy depends on proper normalization and calibration of the measured interferogram. Because only a fraction of light is coupled to the CT spectrometer, a fraction of the signal is lost in this method. Summation of multiple orders produced by the Fabry-Perot etalon may be used to increase the signal-to-background ratio, but was not implemented in the reconstruction discussed in this work. Experimentally, a higher repetition rate laser may be used to reduce the measurement time and further increase the signal-to-background ratio. While such instruments would be invaluable for LIBS measurements requiring accurate isotope ratio measurements, the technique would enable practical instruments for a variety of high-resolution field applications.

LIBS measurements of uranium isotopes using a hybrid spectrometer were made in air and high-resolution uranium wavelength spectra were retrieved. In previous
work by Cremers et al. [30], the isotope shift of uranium was also measured in ambient air. The isotope shift of the 424.437 nm line was observed with spectrometer resolution <10 pm. In uranium measurements made with a DEMON spectrometer (∼6.8 pm resolution) coupled to an ICCD, the 25 pm isotope shift at 424.437 nm was well resolved and the −6 pm isotope shift at 424.167 nm was partially resolved. Each spectrum measured was acquired with 100 laser shots. In that work, an EMU-65 spectrometer (∼10 pm resolution) distinguished between the lines of the 25 pm uranium isotope shift with a non-gated detector, although the each line was pixelated. Each EMU-65 spectrum was an average of 60 laser shots. Because each frame taken lasted approximately 1 s, the collection time was 1 minute per spectrum. In comparison, the resolution achieved by the hybrid interferometric/dispersive spectrometer is similar to the resolution of the DEMON. However, the spectrum taken by a hybrid spectrometer required relatively longer collection times due to decreased transmission, similar to collection times of the EMU-65 for uranium (∼1 min). The current laboratory setup of the hybrid spectrometer is approximately the same size of DEMON and larger than the EMU-65. While the resolution of the instrument is a combination of all of the light detection system, the vast majority of the resolving power is due to the Fabry-Perot etalon. Thus, replacing the 0.55 mm focal length spectrometer of the hybrid device with more compact dispersive device, such as a miniature spectrometer, could substantially reduce the overall size of the instrument and enhance portability without sacrificing performance.

Summation of the entire interference pattern from different lines of uranium produced by the Fabry-Perot etalon may also be able to increase the signal-to-background, but was not implemented due to the partial overlap of the U I 424.626 nm and the U II 424.412 nm lines. With a resolution of ∼6 pm, the hybrid instrument is easily capable of detecting the 25 pm isotope shift at 424.437 nm for uranium in ambient air. However, the 424.167 nm isotope shift, limited by spec-
tral broadening, was only partially resolved. Measurements at reduced pressures or varying gases could further enhance spectral resolution, but were beyond the scope of this study.

7.2 Future work

7.2.1 Characterizing detection sensitivity

![Simulation of uranium spectra](image)

**Figure 7.1.** Simulated fringes of uranium of varying $^{235}$U enrichments: 93% (green), 50% (black), 20% (orange), 7% (red), 0.7% (blue). The source spectrum is assumed to exhibit a 10 pm peak width and a Lorentzian distribution.

Obtaining uranium samples with a range of enrichments was not possible within the limited resources available for this study. As a result, characterization of isotope ratio accuracy of the instrument is recommended for future study. A simulation of the spectra that could be reconstructed using the described method for uranium at varying $^{235}$U enrichments is shown in Figure 7.1. The simulation suggests that the different isotopes ($^{235}$U, $^{238}$U) can be distinguished at a range of
enrichments.

7.2.2 Nuclear material analysis

The hybrid spectrometer may be implemented in measurements of nuclear material (e.g., plutonium) for analysis that benefits safeguards and nonproliferation. Nuclear material may exhibit a number of signatures that reveal information about the purpose or origin of the material. For example, the $^{235}$U/$^{238}$U and $^{239}$Pu/$^{240}$Pu ratios indicate whether a material is weapons grade ($^{235}$U > 90%, $^{240}$Pu < 7%), weapons usable ($^{235}$U > 20%) or reactor grade ($^{235}$U < 20%, $^{240}$Pu > 19%). In nuclear energy applications, isotopes can potentially be used to monitor the burnup rates of fuel to determine if they are in accordance with specifications made in international treaties. Additionally, there are a number of other isotopes from different elements that provide information about reactor operation or reprocessing (e.g., krypton, zirconium, niobium, technetium, ruthenium, iodine, tellurium, xenon, cesium, lanthanum, carbon, sodium, magnesium, iron, cobalt, nickel, copper) that can potentially be monitored using LIBS [5].

7.2.3 Miniaturization

A number of different micromachined Fabry-Perot interferometer designs currently exist [104, 105, 106, 107]. Characterizing different options for a Fabry-Perot spectrometer system is important for determining the advantages that can be incorporated into future designs for compact, high-resolution devices. New spectrometer designs are being developed, such as the G-Fresnel device. The G-Fresnel device combines the functions of a grating and a Fresnel lens into a miniature spectral device that disperses and focuses light. A resolution of $\sim$1 nm can be potentially achieved with a millimeter-sized device [108]. Spectrometers such as the G-Fresnel device can potentially serve as a compact, auxiliary dispersion system for a miniaturized hybrid spectrometer. Even more compact designs for integrated spectrom-
eters on a chip have received attention for their relatively simple manufacturing requirements and their diverse applications [109, 110]. Fabry-Perot etalons have high optical quality and stability and could be incorporated into a high-resolution, miniature spectrometer for LIBS [111]. A proposed acronym for such a device is the D-FENDER (Dual Fabry-Perot Etalon aNd Diffraction Grating for Enhanced Resolution) spectrometer.

7.3 Summary

A hybrid interferometric/dispersive device was proposed for making high-resolution LIBS measurements. Integrating a Fabry-Perot etalon with a dispersive spectrometer has proved to be an inexpensive and effective alternative to 2 m focal length Czerny-Turner or echelle spectrometers for detection of uranium isotopes with LIBS. The instrument is capable of resolving the isotope shift of uranium atomic lines from LIBS emission light, which are not resolvable by the Czerny-Turner spectrometer alone. With high resolution capabilities demonstrated in the laboratory setting, the goal for the future is to develop fully portable, relatively inexpensive, high-resolution LIBS systems for application not only for safeguards, but also in other high-resolution spectroscopy applications.
Safety measures for handling nuclear material

A.1 Experiment procedure

A.1.1 Pre-experiment tasks

1. Wear appropriate personal protective equipment (gloves, lab coat, goggles).

2. Setup radiation sample preparation area.
   - Spread out liner on tabletop.
   - Check battery, then turn on survey meter with gamma or alpha probe attached.

3. Prepare vacuum chamber for analysis.
   - Line bottom of chamber with foil.

A.1.2 Experimental setup

1. Sample alignment.
• Place surrogate sample, for alignment, in chamber.

• Use this to align the beamline to the sample with the HeNe laser through two irises before the chamber.

• Set position of laser on sample using HeNe and by adjusting picomoters.

• Check that laser is focused onto sample.

2. Once experiment preparation is complete, block the laser beam and move the sample holder to the radiation preparation area.

A.1.3 Sample preparation

1. Sample mounting.

• Remove blank sample holder.

• Place uranium sample into chamber.

2. Place sample on translation stage inside chamber.

3. Use HeNe laser to check location of laser on the sample.

A.1.4 Running experiment

1. Place lid onto chamber.

• For atmospheric pressure experiments, run experiment with chamber sealed with lid, then pump the chamber down after the experiment.

A.1.5 Post-experiment survey and cleanup

1. Removing sample.

• Re-pressurize chamber and remove lid.
• Remove sample holder and place onto designated radiation area on preparation surface.

• Remove uranium sample and place it back in its storage area.

• Take a kimwipe and moisten with alcohol, then wipe down sample holder. Place kimwipe in radiation waste bin.

2. Clean experiment area.

• Slowly remove lining foil from chamber by folding it into itself and placing it in the radiation waste bin.

• Take a large kimwipe and moisten with alcohol, then wipe down inside of chamber. Place kimwipe in radiation waste bin.

• Place liner for sample preparation area and any other item that may have been contaminated (gloves, towels, etc.) into radioactive waste bin.

3. Conduct contamination survey of the experiment area and laboratory.

A.2 System safety and radiation protection

The experimental apparatus for LIBS includes a vacuum chamber with multiple viewports for light delivery and transport. The system is connected to a vacuum pump that draws air from the chamber and passes it through a series of two high efficiency particulate (HEPA) filters. This helps prevent particulate matter from reaching the vacuum pump, which vents to the outside of the chamber. The chamber is sealed during the experiment. The chamber is vented and pumped down for three cycles prior to opening the chamber after the experiment, although airborne radioactivity is not expected.

There is a low risk of damage to the radioactive samples during experiment preparation. Transportation of the sample in the laboratory will be minimized to
ensure security and safety. The samples will be sealed and carried in designated sealed plastic containers, and only one sample will be transported at a time. The samples do not undergo dissolution or alteration prior to being analyzed. During the experiment a small volume of material \((3 \times 10^{-9} \text{ cm}^3\text{ per laser shot})\) is removed from the sample surface, but does not re-deposit in the interior of the chamber in detectable quantities. The interior of the sample chamber does not contain parts that could easily damage the sample.

After the experiment a contamination survey will be conducted using a pancake style GM detector attached to a meter (Ludlum Model 3 and 44-9 detector). The area will also be surveyed with an alpha detector (Ludlum model 43-90).
Appendix B

Mathematica code

Initialize

Clear["Global*"
$root = NotebookDirectory[]
$TextStyle = {"Times", 14};
m = 1; cm = 10^{-2}; mm = 10^{-3}; \mu m = 10^{-6}; nm = 10^{-9}; pm = 10^{-12};
Hz = 1; THz = 10^{12}; s = 1;
fs = 10^{-15};

Import measured data

(* Import files *)
rawdat1 = Import[$root <> "313.15nm_1sgate_4000gain_preampl1x_atm_10accums_1_1.txt", "Table"];
rawdat2 = Import[$root <> "313.15nm_1sgate_4000gain_preampl1x_atm_10accums_2_1.txt", "Table"];
rawdat3 = Import[$root <> "313.15nm_1sgate_4000gain_preampl1x_atm_10accums_3_1.txt", "Table"];
rawdat4 = Import[$root <> "313.15nm_1sgate_4000gain_preampl1x_atm_10accums_4_1.txt", "Table"];
rawdat5 = Import[$root <> "313.15nm_1sgate_4000gain_preampl1x_atm_10accums_5_1.txt", "Table"];
(* Import background *)
rawbackground = Import[$root <> "Background_1sgate_4000secexp_preampl1x_atm_10 accums.txt", "Table"];
background = rawbackground[[1;;Length[rawbackground], 3]];
(* Remove background *)
intensity1 = rawdat1[[1;;Length[rawdat1], 3]] - background;
intensity2 = rawdat2[[1;;Length[rawdat2], 3]] - background;
intensity3 = rawdat3[[1;;Length[rawdat3], 3]] - background;
intensity4 = rawdat4[[1;;Length[rawdat4], 3]] - background;
intensity5 = rawdat5[[1;;Length[rawdat5], 3]] - background;
(* Format data *)
FP1 = Partition[intensity1, 1024];
FP2 = Partition[intensity2, 1024];
FP3 = Partition[intensity3, 1024];
FP4 = Partition[intensity4, 1024];
FP5 = Partition[intensity5, 1024];
(* Integrate ring pattern *)
FPROI1 = Transpose[FP1];
FPROI2 = Transpose[FP2];
FPROI3 = Transpose[FP3];
FPROI4 = Transpose[FP4];
FPROI5 = Transpose[FP5];

(* Plot image on ICCD *)
ArrayPlot[FP1 + FP2 + FP3 + FP4 + FP5,
Frame -> True, FrameStyle -> Thick,
LabelStyle -> TextStyle, FrameLabel -> {"Pixel", "Pixel"}]

Calibration of 312.5674 nm line

(* Determine ROI (corresponding to entrance slit) for horizontal integration *)
ROIminc = 440;
ROImaxc = 485;
profile1c = Total[FPROI1[[ROIminc;;ROImaxc]]];
profile2c = Total[FPROI2[[ROIminc;;ROImaxc]]];
profile3c = Total[FPROI3[[ROIminc;;ROImaxc]]];
profile4c = Total[FPROI4[[ROIminc;;ROImaxc]]];
profile5c = Total[FPROI5[[ROIminc;;ROImaxc]]];

(* Normalize intensity *)
profile1c = profile1c/Max[profile1c];
profile2c = profile2c/Max[profile2c];
profile3c = profile3c/Max[profile3c];
profile4c = profile4c/Max[profile4c];
profile5c = profile5c/Max[profile5c];

(* Average spectra and about the center *)
profilec = profile1c + profile2c + profile3c + profile4c + profile5c;
profilec = (profilec + Reverse[profilec])/2;
profilec = profilec/Max[profilec];

ListPlot[profilec, Joined -> True, Axes -> False, PlotRange -> All,
Frame -> True, PlotStyle -> {Black, Thick},
FrameLabel -> {"Pixel", "Intensity (arb.u.)"}, LabelStyle -> TextStyle,
FrameStyle -> Thick, ImageSize -> Medium]
(* Determine pixel positions of interference maxima *)

Position[profilec, Max[profilec[[630;;710]]]]

Position[profilec, Max[profilec[[740;;805]]]]

Position[profilec, Max[profilec[[820;;875]]]]

Position[profilec, Max[profilec[[875;;930]]]]

\{\{360\}, \{665\}\}

\{\{250\}, \{775\}\}

\{\{174\}, \{851\}\}

\{\{113\}, \{912\}\}

Cailbrate angle axis

\[n = 1; \text{(* refractive index*)}\]

\[d = 0.44\text{mm}; \text{(* distance between etalons*)}\]

\[\lambda_c = 312.5674\text{nm}; \text{(* wavelength of calibration line*)}\]

(*Calculateanglesforconstructiveinterference : \(k \sim 2dn/\lambda^2\))

\[k = \text{Round}[2dn/\lambda_c]; \text{(* order f interference for small angles *)}\]

\[\theta_0 = \text{ArcCos}\left[\frac{(k)\pi\lambda_c}{2\pi dn}\right];\]

\[\theta_1 = \text{ArcCos}\left[\frac{(k-1)\pi\lambda_c}{2\pi dn}\right];\]

\[\theta_2 = \text{ArcCos}\left[\frac{(k-2)\pi\lambda_c}{2\pi dn}\right];\]
\[ \theta_3 = \arccos \left( \frac{(k-3)\pi \lambda c}{2\pi dn} \right); \]

(*Calibration data from peak positions and angles corresponding to constructive interference*)

\[ \text{xpix} = \{665, 775, 851, 912\}; (*\text{pixels}*) \]

\[ \text{yangle} = \{\theta_0, \theta_1, \theta_2, \theta_3\}; (*\text{angle (rad)}*) \]

\[
\text{points} = \text{Transpose}\{\text{xpix}, \text{yangle}\}; \\
\text{line} = a \times i + b; \\
\text{fit} = \text{FindFit}\{\text{points}, \{\text{line}\}, \{a, b\}, \text{xi}\}
\]

\[
\begin{align*}
&\{a \rightarrow 0.000131101, b \rightarrow -0.0703568\} \\
&\text{Show}\[\text{Plot}[\text{line}/.\text{fit}, \{\text{xi}, \text{Min}[\text{xpix}], \text{Max}[\text{xpix}]\}, \text{Frame} \rightarrow \text{True}, \text{Axes} \rightarrow \text{False}, \\
\text{PlotStyle} \rightarrow \{\text{Thickness}[0.002], \text{Red}\}, \text{FrameLabel} \rightarrow \{"\text{Pixel}"", "\text{Angle (rad)}"\}, \\
\text{LabelStyle} \rightarrow \$\text{TextStyle}, \text{FrameStyle} \rightarrow \text{Thick}, \\
\text{ListPlot}[\text{points}, \text{PlotRange} \rightarrow \text{All}, \text{Axes} \rightarrow \text{False}, \text{ImageSize} \rightarrow \text{Medium}, \\
\text{PlotStyle} \rightarrow \{\text{PointSize}[0.01], \text{Black}\}]]
\end{align*}
\]
Determine etalon reflectivity

(* Determine region of ring profile for analysis *)
fringeROIminc = 620;
fringeROImaxc = 710;
anglec = Table[line/.fit,
{x, fringeROIminc, fringeROImaxc}];

profilenewc = profilec[[fringeROIminc;;fringeROImaxc]];

Measured =
ListPlot[Transpose[{anglec, profilenewc/Max[profilenewc]}], Joined \[RightArrow] True,
Axes \[RightArrow] False, PlotRange \[RightArrow] All,
Frame \[RightArrow] True, PlotStyle \[RightArrow] {Thick, Black},
FrameLabel \[RightArrow] {"Angle (rad)", "Intensity (arb.u.)"}, LabelStyle \[RightArrow] TextStyle,

Cal = Transpose[{anglec, profilenewc}];

Frame \[RightArrow] True, PlotStyle \[RightArrow] Black,
FrameLabel \[RightArrow] {"", "Intensity (a.u.)"}, LabelStyle \[RightArrow] TextStyle,
FrameStyle \rightarrow \text{Thick};

(* Define etalon parameters *)

\(n = 1;\) (* refractive index *)

\(d = 0.44\text{mm};\) (* distance between etalons *)

\[
\text{calmodel} = \frac{A}{1 + \left(\frac{\text{refl}}{1-\text{refl}^2}\right)^2 \sin \left[\frac{2\pi}{dn} \text{dn}[\text{calvars}] + \phi\right]^2} + \text{bkg};
\]

\[
\text{calconstraints} = \{A > 0, \text{bkg} > 0\};
\]

\[
\text{calvars} = \{\{A, 1\}, \text{bkg}, \text{refl}, \phi\};
\]

\[
\text{calfit} = \text{FindFit}[\text{Cal}, \{\text{calmodel, calconstraints}\}, \text{calvars}, \text{xi}]
\]

\text{Show[}
\text{ListPlot}[\text{Cal}, \text{PlotRange} \rightarrow \text{All}, \text{ImageSize} \rightarrow \text{Medium}, \text{Axes} \rightarrow \text{False},
\text{PlotStyle} \rightarrow \{\text{PointSize}[0.01], \text{Black}\}, \text{Frame} \rightarrow \text{True},
\text{FrameLabel} \rightarrow \{"\text{Angle (rad)}", "\text{Intensity (arb.u.)}\"\}, \text{LabelStyle} \rightarrow \$\text{TextStyle},
\text{FrameStyle} \rightarrow \text{Thick},
\text{Plot[calmodel/.calfit, \{xi, anglec[[1]], anglec[[Length[anglec]]]}], \text{PlotRange} \rightarrow \text{All},
\text{Axes} \rightarrow \text{False}, \text{ImageSize} \rightarrow \text{Medium}, \text{PlotStyle} \rightarrow \{\text{Thickness}[0.002], \text{Red}\}]
\text{]}
\text{\{A \rightarrow 0.971531, \text{bkg} \rightarrow 0.0123133, \text{refl} \rightarrow 0.890397, \phi \rightarrow 0.01439\}}
Analysis of 313 nm doublet

(* Determine ROI corresponding to entrance slit for horizontal integration *)
ROImin = 490;
ROImax = 535;

profile1 = Total[FPROI1[[ROImin;;ROImax]]];
profile2 = Total[FPROI2[[ROImin;;ROImax]]];
profile3 = Total[FPROI3[[ROImin;;ROImax]]];
profile4 = Total[FPROI4[[ROImin;;ROImax]]];
profile5 = Total[FPROI5[[ROImin;;ROImax]]];

(* Normalize intensity *)
profile1 = profile1/Max[profile1];
profile2 = profile2/Max[profile2];
profile3 = profile3/Max[profile3];
profile4 = profile4/Max[profile4];
profile5 = profile5/Max[profile5];
(* Average spectra and averaged about the center *)

profile = profile1 + profile2 + profile3 + profile4 + profile5;
profile = profile + Reverse[profile]/2;
profile = profile/Max[profile];
length = Length[profile];

ListPlot[profile, Joined -> True, Axes -> False, PlotRange -> All,
Frame -> True, PlotStyle -> {Black, Thick},
FrameLabel -> {"Pixel", "Intensity (arb.u.)"}, LabelStyle -> $TextStyle,
FrameStyle -> Thick, ImageSize -> Medium]

(* determine position and intensities of 313.1844 nm lines *)

Position[profile, Max[profile[[140;;150]]]]
Max[profile[[140;;150]]]/N
Position[profile, Max[profile[[205;;225]]]]
Max[profile[[204;;220]]]/N
Position[profile, Max[profile[[290;;315]]]]
Max[profile[[290;;315]]]/N
{{145}, {880}}

0.64111
Determine gaussian envelope function

\[
xgauss = \{145, 214, 304, 721, 811, 880\};
\]
\[
ygauss = \{0.64242, 0.762964, 1.0, 1.0, 0.762964, 0.64242\};
\]
\[
ygauss = ygauss/Max[ygauss];
\]
ListPlot
[Transpose[{xgauss, ygauss}], Frame \[\rightarrow\] True, Axes \[\rightarrow\] False, PlotRange \[\rightarrow\] All, PlotStyle \[\rightarrow\] {Thick, Black}, Joined \[\rightarrow\] False, FrameLabel \[\rightarrow\] {"Angle \(\theta\) (mrad)", "Wavelength (nm)"},] LabelStyle \[\rightarrow\] TextStyle, FrameStyle \[\rightarrow\] Thick];

Calgauss = Transpose[{xgauss, ygauss}];

calmodelgauss = \(A \exp \left[\frac{-(x-b)^2}{\Delta x^2}\right] + bkg\);

calconstraintsgauss = \{b > 0, \Delta x1 > 0\};
calvarsgauss = \{\{b, 512\}, \{\Delta x1, 200\}, \{A, 1\}, bkg\};
calfitgauss =
FindFit[Calgauss, \{calmodelgauss, calconstraintsgauss\}, calvarsgauss, xi]

calibrationplotgauss = Show[
ListPlot[Calgauss, PlotRange \[\rightarrow\] All, ImageSize \[\rightarrow\] Medium, Axes \[\rightarrow\] False, PlotStyle \[\rightarrow\] {PointSize[0.01], Black}, Frame \[\rightarrow\] True, FrameStyle \[\rightarrow\] Thick, FrameLabel \[\rightarrow\] {"Pixel", "Intensity (arb.u.)"}, LabelStyle \[\rightarrow\] TextStyle, Plot[calmodelgauss/.calfitgauss, \{xi, 0, 1024\}, PlotRange \[\rightarrow\] All, Axes \[\rightarrow\] False, ImageSize \[\rightarrow\] Medium, PlotStyle \[\rightarrow\] {Thickness[0.002], Red}]]]
\{b \rightarrow 512.498, \Delta x_1 \rightarrow 258.858, A \rightarrow 0.9182, \text{bkg} \rightarrow 0.52006\} 

\begin{align*}
\text{Pixel} & \quad 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \\
\text{Intensity (arb.u.)} & \quad 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 
\end{align*}

(* Define distribution function *)

gauss = \text{Table} \left[ \frac{\text{calmodelgauss} / \text{calfitgauss}}{\text{xi}}, \{\text{xi}, 0, 1024\} \right] ;

gprofile = \text{profile} / \text{gauss};

\text{ListPlot}[gprofile, \text{Joined} \rightarrow \text{True}, \text{Axes} \rightarrow \text{False}, \text{PlotRange} \rightarrow \text{All},
\text{Frame} \rightarrow \text{True}, \text{PlotStyle} \rightarrow \{\text{Black, Thick}\},
\text{FrameLabel} \rightarrow \{"\text{Pixel}"}, "\text{Intensity (arb.u.)}"\},
\text{LabelStyle} \rightarrow \$\text{TextStyle}, \text{FrameStyle} \rightarrow \text{Thick}\]
Reconstruct source spectrum

(* Define region of interference pattern profile for analysis *)
fringeROImin = 675;
fringeROImax = 790;

profilenew = profile[[fringeROImin;;fringeROImax]];
angle = Table[line/.fit, {xi, fringeROImin, fringeROImax}];
nsample = Length[profilenew];

ListPlot[Transpose[{angle, profilenew/Max[profilenew]}], Joined -> True,
Axes -> False, PlotRange -> All,
Frame -> True, PlotStyle -> {Black, Thick},
FrameLabel -> {"Angle (rad)", "Intensity (arb.u.)"}, LabelStyle -> $TextStyle,
FrameStyle -> Thick, ImageSize -> Medium]

(* Defining 2D instrument function *)
\[\lambda_1 = 313.1555\text{nm};\]
\[\lambda_2 = 313.1844\text{nm};\]
\[r = 0.89;\] (* determined etalon reflectivity *)
\[\lambda_t = \text{Table}[i, \{i, (\lambda_1 - 0.05\text{nm}), (\lambda_2 + 0.05\text{nm}), \frac{(\lambda_2+0.05\text{nm})-(\lambda_1-0.05\text{nm})}{\text{nsample}-1}\}];\]
(* define wavelength axis *)

\[
\theta_t = \text{angle} \; (* \text{define angular axis} *)
\]

\[
T_t = \text{Outer} \left[ \frac{1}{1 + \left( \frac{2}{1 - \alpha^2} \right)^2 \frac{\sin \left[ 2 \pi \frac{\alpha}{1 - \alpha^2} \right]}{\sin \left[ \frac{\pi}{\theta_t} \right]} \right], \lambda t, \theta_t \right];
\]

(* construct 2D instrument function *)

\[
\text{ArrayPlot}[T_t, \text{Frame} \rightarrow \text{True}, \text{FrameStyle} \rightarrow \text{Thick}, \text{LabelStyle} \rightarrow \$\text{TextStyle}, \\
\text{FrameLabel} \rightarrow \{"\text{Angle (rad)}", "\text{Wavelength (nm)}"\}]
\]

(* incorporate \(\alpha\) factor for reflectivity *)

\[\alpha = 1.07;\]

\[r_{\text{new}} = \alpha 0.89;\]

\[
T_{\text{tnew}} = \text{Outer} \left[ \frac{1}{1 + \left( \frac{2r_{\text{new}}}{1 - r_{\text{new}}^2} \right)^2 \frac{\sin \left[ 2 \pi \frac{\alpha}{1 - \alpha^2} \right]}{\sin \left[ \frac{\pi}{\theta_t} \right]} \right], \lambda t, \theta_t \right];
\]

\[
\text{ArrayPlot}[T_{\text{tnew}}];
\]

(* Define tolerance level for least squares *)

\[\text{Tol} = 0.05;\]

\[
\text{reconstruct} = \text{PseudoInverse}[\text{Transpose}[T_{\text{tnew}}], \text{Tolerance} \rightarrow \text{Tol}].\text{profilenew};
\]
reconstruct = reconstruct/Max[reconstruct];

(* Spectrum reconstructed using least squares analysis *)
ListPlot[Transpose[{λtnew/nm, reconstruct}], PlotRange -> All, Joined -> True,
Axes -> False, PlotRange -> All,
Frame -> True, PlotStyle -> {Black, Thick},
FrameLabel -> {"Wavelength (nm)", "Intensity (arb.u.)"},
LabelStyle -> $TextStyle, FrameStyle -> Thick]

Interpolate and resample

Off[InterpolatingFunction::"dmval"];
Aw1 = Transpose[{angle, profilenew}];
Aint1 = Interpolation[Aw1, InterpolationOrder -> 1];

Plot[Aint1[i], {i, Min[anglenew], Max[anglenew]},
Frame -> True, PlotRange -> All, Axes -> False, PlotStyle -> {Thick, Black},
FrameLabel -> {"Angle θ (rad)", "Wavelength (nm)", "Interpolation"},
LabelStyle -> $TextStyle, FrameStyle -> Thick]
Interpolation

Wavelength (nm)

0.2
0.4
0.6
0.8
1.0

Angle Θ (rad)

0.022 0.024 0.026 0.028 0.030

nsamplen = 2^{10};

(* must be even *)

θ\text{minn} = \text{Min}[\text{anglenew}]; \theta\text{maxn} = \text{Max}[\text{anglenew}];

δθ = (\theta\text{maxn} − \theta\text{minn})/\text{nsamplen};

θ\text{newtoo} = \text{Table}[\theta\text{minn} + δθi, \{i, 1, \text{nsamplen}\}];

A1\text{resample} = 
\text{Table}[\text{If}[θ\text{newtoo}[i] ≤ \text{Max}[\text{anglenew}] && \theta\text{newtoo}[i] ≥ \text{Min}[\text{anglenew}], 
\text{A1}[θ\text{newtoo}[i]], 0], \{i, 1, \text{nsamplen}\}];

Aω1\text{replot} = \text{Transpose}[\{θ\text{newtoo}, \text{A1resample}/\text{Max}[\text{A1resample}]\}];

(* Define new 2D instrument function *)

λ\text{resample} = 
\text{Table}[[i, \{i, (λ1 − 0.05\text{nm}), (λ2 + 0.05\text{nm}), \frac{(λ2+0.05\text{nm})−(λ1−0.05\text{nm})}{\text{nsamplen}−1} \}]] ;

θ\text{tresample} = 
\text{Table}[i, \{i, \text{anglenew}[1], \text{anglenew}[\text{Length}[\text{anglenew}]], 
\frac{\text{anglenew}[\text{Length}[\text{anglenew}]]−\text{anglenew}[1]}{\text{nsamplen}−1} \}]] ;
\[ T_{\text{resample}} = \text{Outer} \left[ \frac{1}{1 + \left( \frac{2r_{\text{new}}}{1 - r_{\text{new}}} \right)^2 \sin \left( \frac{\pi}{4} d n \cos \theta \right)} \& , \lambda_{\text{sample}}, \theta_{\text{resample}} \right] ; \]

ListPlot[Transpose[{\theta_{\text{resample}}, A1_{\text{resample}}}],
PlotRange -> All, Joined -> True,
Frame -> True, PlotRange -> All, Axes -> False, PlotStyle -> {Thick, Black},
FrameLabel -> {"Angle \(\theta\) (rad)", "Wavelength (nm)", "Resampled"},
LabelStyle -> $TextStyle, FrameStyle -> Thick]

\[ \text{Reconstruct}_{\text{resampled sourcespectrum}} \]

Toln = 0.05; (* Define tolerance level for least squares *)
resampreconstruct =
PseudoInverse[Transpose[Ttresample], Tolerance -> Toln].A1resample;
resampreconstruct = resampreconstruct/Max[resampreconstruct];

ListPlot[Transpose[{\lambda_{\text{sample}}/\text{nm}, resampreconstruct}],
PlotRange -> All,
Joined -> True, Axes -> False, PlotRange -> All,
Frame -> True, PlotStyle -> {Black, Thick},
FrameLabel -> {"Wavelength(nm)", "Intensity(\text{arb. u.})"},
LabelStyle -> $TextStyle, FrameStyle -> Thick]


HPGe analysis of uranium foils

C.1 Introduction

The uranium foils used for experiments were legacy samples from the Penn State University’s Breazeale Nuclear Reactor. Gamma spectra was acquired by a High-Purity Germanium detector to further characterize the samples. Enrichment was obtained from gamma spectra by using the Multi-Group Analysis for Uranium (MGAU) technique.

Traditional methods deduce the enrichment from the intensity of the $^{235}\text{U}$ 186 keV peak, which is emitted after $^{235}\text{U}$ decays by alpha decay to $^{231}\text{Th}$. However, these methods require that samples meet the infinite thickness criterion; the uranium sample being analyzed must be at least $\sim$0.26 cm thick. The infinite thickness is estimated to be 7 times the mean free path of the 186 keV photon in uranium metal (density: $\sim$18.7 g/cm$^3$) which is $\sim$0.04 cm. The mean free path is defined as the absorber thickness that reduces the gamma ray intensity to $1/e$, and is equal to the average distance that a gamma ray travels before interacting with the absorber. The sample should be spatially homogeneous, and detector calibration should be performed with a well characterized calibration sample with the same geometry as the unknown sample [112]. A peak ratio technique for
distinguishing natural from highly-enriched uranium that compares the 186 keV peak to the $^{238}\text{U}$ daughter ($^{234}\text{mPa}$) 1001 keV photopeak is not applicable in our measurements because the High-purity Low-Energy Germanium (LEGe) detector used in our experiments was optimized for photons in the low energy spectrum below 300 keV [113].

![Gamma spectrum of uranium sample](image)

**Figure C.1.** Example gamma spectrum of a uranium sample with 4.46% enrichment. The energy region shown is analyzed by MGAU with response functions representing contributions of different uranium isotopes [114].

The thicknesses for the natural and highly-enriched uranium foils are 0.26 mm and 0.11 mm, respectively, and did not meet the criterion for the Infinite Thickness Method. Furthermore, the foil geometries differed greatly and there were no suitable standards that available for calibration.

The MGAU approach was chosen to estimate the sample enrichment because it is relatively insensitive to the sample matrix or measurement geometry. An example of the MGAU technique applied to a uranium spectrum is shown in Figure C.1. The abundance of one isotope is related to the measured line strength of the isotope, as described in the equation

$$i = \Lambda a b \Omega \varepsilon \tau,$$

(C.1)
where $i$ is the measured line strength in counts per minute, $\Lambda$ is the decay constant of that isotope, $a$ is the number of atoms in the isotope, $b$ is the branching ratio of the isotope, $\Omega$ is the fractional solid angle of the detector, $\varepsilon$ is the counting efficiency of that isotope and $\tau$ is the gamma transmission. The ratio of isotopes 1 and 2, $a_1/a_2$, can be estimated by \(\frac{(i_1 \Lambda_2 b_2 \Omega_2 \varepsilon_2 \tau_2)}{(i_2 \Lambda_1 b_1 \Omega_1 \varepsilon_1 \tau_1)}\). The detector efficiencies and gamma transitions in the ratio $\varepsilon_2 \tau_2/\varepsilon_1 \tau_1$ for different gamma and x-rays need to be determined in order to estimate the isotope ratio. The fractional solid angle of the detector can be assumed to be the same for both isotopes ($\Omega_1 \simeq \Omega_2$) [115]. MGAU uses an advanced algorithm to analyze closely spaced X-ray and gamma ray photopeaks in a uranium spectrum and generates an intrinsic energy efficiency calibration to estimate the enrichment of an unknown sample. It is assumed that $^{234}$Th is in equilibrium with its parent $^{238}$U in the sample [114].

A Canberra liquid nitrogen cooled LEGe with a Canberra Inspector 2000 multi-channel analyzer (MCA) and Genie 2000 software is used to measure the gamma ray spectra of the uranium foils. The software used for obtaining the uranium enrichment of the foils is MGAU (version 4.2).

### C.2 Results

The MGAU method was applied to gamma spectra of uranium foils and yielded 0.7% enrichment for the natural uranium foil and 96% for highly-enriched uranium foil, which agree with reported values and indicate a large difference in enrichment between the two samples. The natural foil was counted for 41.7 minutes (0.2% dead time) and highly-enriched uranium was counted for 16.7 minutes (2% dead time). Figure C.2 and Figure C.3 show regions of the spectrum and peaks that were used in the analysis. Figure C.4 and Figure C.5.
Figure C.2. Gamma spectrum showing several peaks used in MGAU analysis in the 50–150 keV energy region. The photopeaks used in the analysis are ThKα₁ at 93.4 keV (1), UKα₂ at 94.7 keV (2), UKα₁ at 98.4 keV (3), UKβ₁ at 111.3 keV (4) and γ²³⁵⁵U at 143.7 keV (5) [114]. Characteristic 63.35 keV ²³⁴Th (²³⁸U daughter) gamma peak is labeled. Spectra are offset to show differences.

Figure C.3. Gamma spectrum showing several peaks used in MGAU analysis in the 150–220 keV energy region. The photopeaks used in the analysis are γ²³⁵⁵U at 163.4 keV (6), γ²³⁵⁵U at 185.7 keV (7), γ²³⁵⁵U at 202.1 keV (8) and γ²³⁵⁵U at 205.3 keV (9) [114]. Spectra are offset to show differences.
<table>
<thead>
<tr>
<th>Energy, keV</th>
<th>Counts</th>
<th>Rel. Efficiency</th>
<th>Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.4</td>
<td>791</td>
<td>1.825</td>
<td>4.56</td>
</tr>
<tr>
<td>94.7</td>
<td>4206</td>
<td>1.806</td>
<td>2.54</td>
</tr>
<tr>
<td>98.4</td>
<td>6461</td>
<td>1.737</td>
<td>2.24</td>
</tr>
<tr>
<td>111.3</td>
<td>1351</td>
<td>1.608</td>
<td>3.72</td>
</tr>
<tr>
<td>143.7</td>
<td>1136</td>
<td>1.357</td>
<td>3.97</td>
</tr>
<tr>
<td>163.4</td>
<td>458</td>
<td>1.180</td>
<td>5.67</td>
</tr>
<tr>
<td>185.7</td>
<td>4370</td>
<td>1.000</td>
<td>2.51</td>
</tr>
<tr>
<td>202.1</td>
<td>65</td>
<td>0.783</td>
<td>13.44</td>
</tr>
<tr>
<td>205.3</td>
<td>295</td>
<td>0.771</td>
<td>6.82</td>
</tr>
</tbody>
</table>

Figure C.4. MGAU results for natural uranium foil.

<table>
<thead>
<tr>
<th>Energy, keV</th>
<th>Counts</th>
<th>Rel. Efficiency</th>
<th>Uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.4</td>
<td>51494</td>
<td>1.699</td>
<td>1.44</td>
</tr>
<tr>
<td>94.7</td>
<td>28917</td>
<td>1.698</td>
<td>1.59</td>
</tr>
<tr>
<td>98.4</td>
<td>45390</td>
<td>1.669</td>
<td>1.47</td>
</tr>
<tr>
<td>111.3</td>
<td>10183</td>
<td>1.657</td>
<td>1.99</td>
</tr>
<tr>
<td>143.7</td>
<td>81529</td>
<td>1.392</td>
<td>1.35</td>
</tr>
<tr>
<td>163.4</td>
<td>32386</td>
<td>1.193</td>
<td>1.56</td>
</tr>
<tr>
<td>185.7</td>
<td>305758</td>
<td>1.000</td>
<td>1.18</td>
</tr>
<tr>
<td>202.1</td>
<td>5080</td>
<td>0.880</td>
<td>2.40</td>
</tr>
<tr>
<td>205.3</td>
<td>23064</td>
<td>0.862</td>
<td>1.66</td>
</tr>
</tbody>
</table>

Figure C.5. MGAU results for highly-enriched uranium foil.
Bibliography


and ablation thresholds for metals and dielectrics,” *Physics of Plasmas*, 9, 949-957.


Vita

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2010 Henry Rutgers Senior Thesis Award
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The Effect of Nitric Acid on Cloud Processing of Glyoxal