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BARIUM CONCENTRATIONS IN ROCK SALT BY LASER INDUCED BREAKDOWN SPECTROSCOPY

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BREAKDOWN SPECTROSCOPY

By

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Abstract

Time-REsolved Laser Induced Breakdown Spectroscopy (TRELIBS) was used to determine the elemental concentration of barium in Texas Dome rock salt. TRELIBS allows for an efficient and *in situ* concentration analysis technique that detects a wide range of elements with no sample preparation.

TRELIBS measurements were made in the 545nm to 594nm wavelength range. The proximity of a strong barium emission line (553.5481 nm) to the sodium doublet (588.9950 nm and 589.5924 nm) allowed for measurement within a single frame of the spectrograph.

This barium emission line was compared to the sodium doublet for relative intensity. A homemade calibration sample containing known amounts of barium and sodium was used to determine the relative concentrations. By approximating the sodium content in the rock salt as 50%, we determined the absolute concentration of barium in the salt to be $(0.13\pm0.03)\%$.

1   Introduction

Salt is produced in three ways: solar evaporation, rock salt mining, and vacuum evaporation. Rock salt mining accounts for approximately a third of salt production worldwide, but is less pure when compared to the other methods. [1] Purifications of 99-99.5% and 99.8-99.95% NaCl can be achieved for solar salt and vacuum evaporation salt (respectively). Rock salt purity ranges from 97-99+%. [1]

Rock salt, or Halite, is naturally occurring worldwide, with several well-studied mines throughout the United States and Europe [2]. Rock salt is heavily used in deicing roads in snowbelt regions, which accounts for approximately 10% of worldwide salt consumption [1]. There are environmental consequences linked to the use of salt as a deicing agent, including contamination that could affect plant and animal life [3]. The trace elements in the rock salt become of concern when this salt has seeped into the ground or nearby water sources, potentially polluting the groundwater or other drinking supplies. As a result, it is important to know the composition and concentration of trace elements in rock salt.

Presently, the analysis of rock salt requires a multi-step process that typically involves dissolving the solution into brine, removing water insoluble materials by stirring, and only then proceeding with subsequent analysis [4]. This preparation alone is slow-paced and must be performed in a laboratory. A technique that is *in situ*, efficient, and requires no sample preparation would be valuable to the salt mining industry. An early-stage analysis technique such as Time Resolved Laser Induced Breakdown Spectroscopy (TRELIBS) would allow for companies to plan which purification measures are required for a particular salt sample.

Barium is a regularly occurring pollutant in rock salt. Most commonly, Barium is commercially used in its sulfate form, which is water insoluble and can be ingested without consequences. However, in raw elemental form, Barium is harmful when consumed. For this reason it will be examined in this thesis report. It should also be noted that TRELIBS identifies a large range of elements, and thus the technique is not limited to the detection of Barium.

2   Theory

2.1   TRELIBS: Time-Resolved Laser Induced Breakdown Spectroscopy

TRELIBS uses a high energy pulse laser to create hot plasma by multiphoton ionization at the surface of the sample. The highly ionized gas from the plasma ablates and consequently dissociates molecules in the surrounding material into ions and free atomic species. These atomic species recombine with electrons as the plasma cools and emit characteristic radiation for up to tens of microseconds [5]. Emission can also be produced from neutral electron impact excitation. The emission is then detected by a spectrograph and compiled into a wavelength spectrum. The spectrum can then be export and analyzed for relative and absolute concentration analysis.

There are several advantages of TRELIBS that are ideal for field spectroscopic analysis. TRELIBS detects a wide range of elements simultaneously. Ablation is a consequence of the plasma, which is produced by any high power laser. As a result, the wavelength of the laser does not directly affect the excitation of the elemental species. This provides TRELIBS with an advantage over Laser Induced Fluorescence (LIF), which requires a tunable laser to induce excitation [6]. With TRELIBS, detection of multiple elements is possible simultaneously, allowing for a comprehensive composition analysis.

The plasma decomposes every part of the sample into elemental components, regardless of atmosphere or matrix composition. Consequently, samples analyzed with TRELIBS require minimal to no sample preparation. This allows for samples to be analyzed immediately in the field, instead of requiring transportation to a laboratory

setting. In addition, TRELIBS can produce useable, high resolution spectra within a matter of seconds.

Since the plasma is created by focused light, a portable setup of TRELIBS can be designed for convenient use in the field. Such equipment already exists, most notably the ChemCam Instrument Suite on the Mars Science Laboratory (MSL) Rover ("Curiosity") [7]. With these considerations (wide range of detection, no sample preparation, and fast data collection), TRELIBS is incredibly beneficial and efficient for *in situ* analysis.

2.2   Time Resolution

While electrons are combining with ions to produce characteristic radiation, there are also species of electrons that are not captured by the ions. These 'free' electrons decelerate through collisions and cause a bremsstrahlung background radiation [8]. Typically, this continuum is much larger than the atomic emission of trace elements [5], and as a result the atomic spectral features tend to be overwhelmed by the bremmstrahlung background. Since the bremmstrahlung and the atomic emission occur at the same frequency, it is impossible to use a filter to filter out the continuum. Instead, a time delay is introduced between the time the plasma ablates the sample and the time of data collection to maximize the detection of the atomic emission and minimize the background continuum. Thus, the bremsstrahlung continuum becomes much less intense after the time delay, allowing for optimized signal-to-noise detection of the atomic emission.
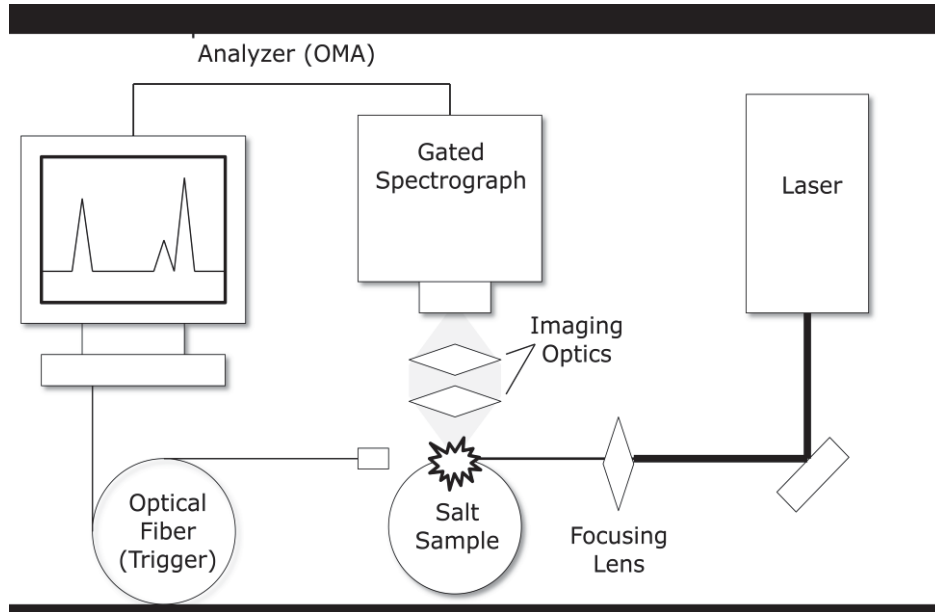
3 Experiment

Figure 1: Optical tabletop TRELIBS setup.

3.1 Experimental Setup

For the experiment (Figure 1), the second harmonic of a pulsed Nd:YAG laser

was focused on the Texas Hockley Dome raw rock salt sample to initiate the breakdown

described in Section 2, Theory. The laser had a wavelength of 532nm, pulse duration of

10ns, typical pulse energy of 300mJ, and a rate of repetition of 10Hz. The laser light was

focused by a lens (focal length ~17cm) onto the salt surface. The focusing lens was

positioned such that the plasma breakdown was induced at a right angle to the 275mm

crossed Czerny-Turner gated spectrograph with a grating of 1200 lines/mm, and an

effective resolution of 0.41nm.

A two lens system of focal length ~5cm and ~9cm, respectively, was placed

between the salt and the spectrograph in order to image maximum light onto the

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spectrograph slit. These lenses were selected such that the imaging optics matched the spectrograph f# of 4.5. The imaged light would shift from the spectrograph slit as repeated laser pulses formed a small crater at the sample surface. The two lens system would be adjusted periodically in order for the light to enter the spectrograph slit.

The Optical Multichannel Analyzer (OMA) was triggered by the laser light through a fiber optic cable. This cable was positioned beyond the salt sample, such that the same laser light that began the breakdown would subsequently trigger the system. This began the time delay and gate width acquisition, which were times specified by the user (see Section 3.2, Time Delay and Gate Width Optimization). The details of the data acquisition protocol are described in the Appendix.

3.2   Time Delay and Gate Width Optimization

The time delay and gate width parameters in the proprietary software Data Acquisition Design (DAD) were varied until the signal-to-noise ratio was optimal. The parameters were considered ideal when the barium peak was maximized, which coincided with a maximal sodium doublet.

Figure 2 shows the evolution of spectral features as time delay is varied. The broad peak at ~560nm disappears as the time delay is increased from 15μs to 30μs. This peak is most likely a calcium emission, and the broadness can be attributed to additional emissions occurring in that range. The peak occurring at ~570nm is most likely a silicon emission, and ~590nm is the sodium doublet [9]. The relative intensities between these peaks vary with the time delay; thus, a single time delay must be selected for measurement and calibration as the spectra evolve with time.
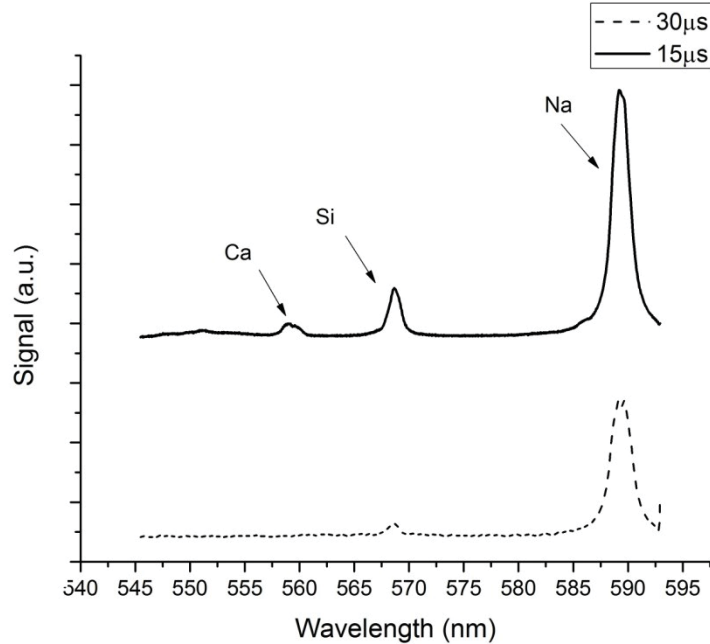
Figure 2: Evolution of TRELIBS spectral features with time delay of 15μs (top, solid line) and 30μs (bottom, dashed line).

The gate width was optimized such that the atomic emission of barium would appear above the dark noise. If the gate was open longer than necessary, detector dark noise would continue to add counts to the spectrum even after the atoms stopped radiating. The dark noise is only minimized once the gate has closed and voltage is no longer applied to the detector. Consequently, an optimization is required such that the gate is open long enough to collect maximum barium emission, but not so long that the dark noise buries the barium peak in background.

The time delay and gate width were found to produce the best signal-to-noise ratio at 15μs and 5μs, respectively.
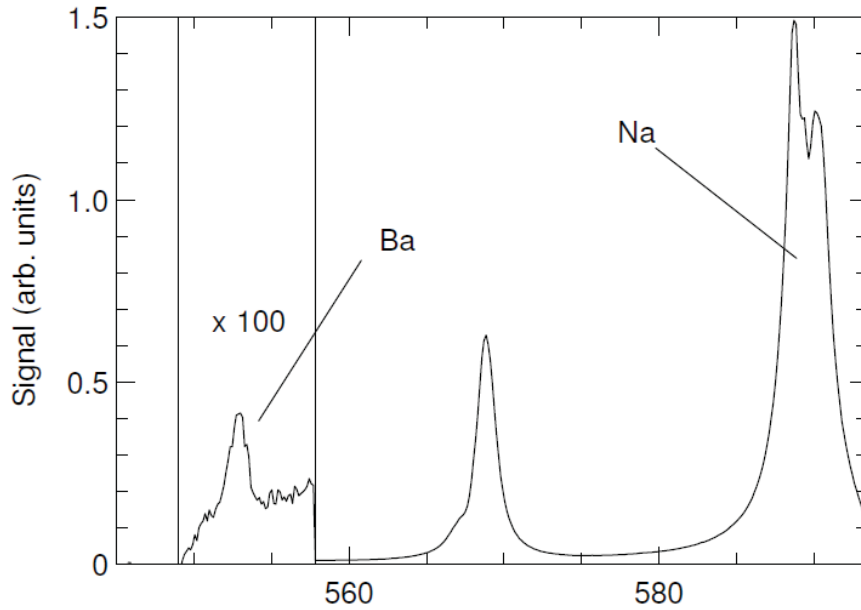
3.3   Data Collection

Figure 3: TRELIBS Spectrum of salt sample. Barium peak is small compared to the sodium doublet and as a result zoom is required to view.

Measurements were taken in the 545nm to 594nm range because of a known barium emission line at 553.5481nm and the sodium doublet at 588.9950nm and 589.5924nm [9]. The closeness of these peaks allowed for measurements to be taken in a single frame of the spectrograph.

Ten iterations of TRELIBS were run from sequential laser pulses to produce a single data acquisition spectrum. This number of iterations was chosen to further optimize the barium and sodium peaks above the dark noise.

The barium peak was observed at 552.8nm and the sodium doublet was observed at 588.7nm and 590.4nm. Another peak was observed at 568.8nm; this is most likely another sodium emission line.

The signal from the sodium doublet had an intensity that saturated the detector. The saturation occurred at intensities of approximately 150,000 counts. A neutral density

filter (Oriel 59340, with nominal optical density 0.50) was introduced to uniformly lower the intensity of light entering the spectrograph. Both the sodium doublet and the barium peak were observed after the introduction of the filter, with the sodium having a new intensity of approximately 148,000 counts (Figure 3).

3.4 Wavelength Calibration

The grating in the spectrograph was rotated such that specific wavelength ranges could be detected. However, the OMA does not automatically account for manual changes of the spectrograph wavelength range, and requires a user-input calibration. A mercury lamp was used to determine the wavelength axis. Mercury has a subset of three strong peaks in the 540nm-590nm range, occurring at 543.07nm, 576.96nm, and 579.84nm [9]. Due to the linear dispersion of the grating, these three peaks were fit with a linear function to determine the wavelength axis.

3.5 Calibration of Relative Intensities

Since the observed transitions of sodium and barium radiate differently, the relative intensities do not necessarily directly correspond to relative concentrations. Consequently, a calibration must be used to determine absolute concentrations for relative intensities of barium and sodium.

Calibration was performed with two homemade samples. Both samples were constructed with a matrix of concrete (brand: QUIKRETE) in order to create a solid sample. QUIKRETE is a Portland cement, and is primarily composed of silica, alumina, limestone, and iron oxide [10]. One sample was mixed with water and left to dry. The

other sample was mixed with 3.49g of Sodium Bismuthate and 3.02g Barium Sulfate.

These weights were chosen because they produce approximately the same atomic

concentration; 0.0117 moles of Barium Sulfate and 0.0129 moles of Sodium Bismuthate.

The chemicals were distributed through the dry QUIKRETE matrix, water was added,

and the sample was set to dry.

Sodium Bismuthate and Barium Sulfate were selected as chemical additives based

on their water insoluble characteristic; this would ensure that there was no chemical

reaction between the matrix and the additives that may result in the creation of ions. If

ions are created and sustained in the calibration sample, different ionized energy levels

would be created in the TRELIBS process, consequently producing a different emission

spectrum than the neutral atom. Were a chemical reaction to occur during the mixing

process, it would be impossible to know how much neutral barium remains and how

much becomes an ion. This renders the calibration difficult for absolute concentrations.

However, when the additives are water insoluble, no chemical reaction occurs and the

additives remain neutral.

The sample without additives was used to observe the matrix background. There

were small amounts of barium detected in the matrix composition. A large peak is present

in the range of the sodium doublet (Figure 4). This large peak does not behave the same

way as the sodium doublet observed in the salt sample, and as a result is not believed to

be the sodium emission line. There are several iron emission lines in the 588nm-590nm

range, including a strong FeII transition that occurs at 588.50162nm. This FeII line has an

Einstein coefficient of 6.4e+07 s^{-1}, which indicates a high transition probability. Due to

the iron content in Portland cement (~6%) [10], this is most likely the transition we are observing.

Spectra of the sample with additives were taken at the same time delay and gate width as the salt sample (15μs and 5 μs, respectively). Seven spectra taken a different locations of the sample were averaged to account for any non-uniform distribution in the sample. Each of these spectra had a different total intensity, so they were first normalized to the calcium peak occurring at 558.8nm. This peak was chosen since the calcium is fully from the matrix.
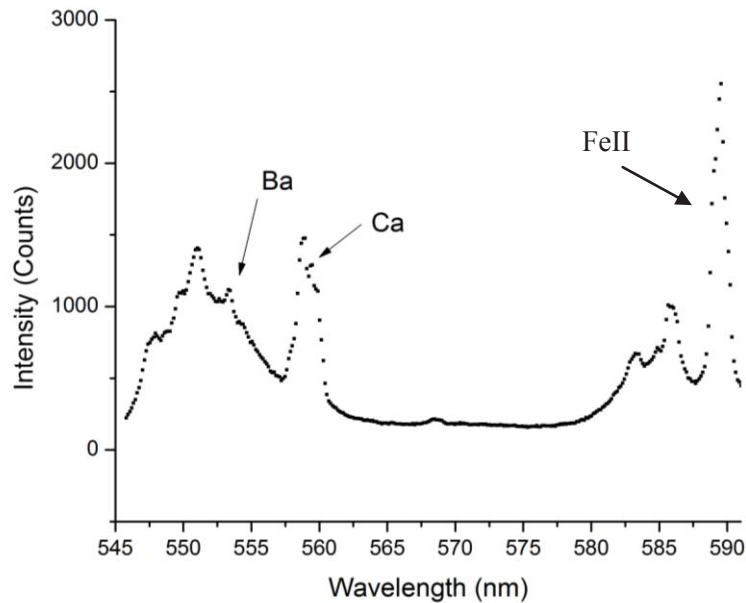

Figure 4: TRELIBS spectrum of QUIKRETE matrix

The barium peak was fit with a Lorentz profile (Figure 5) which resulted in an integrated intensity of 1350±340 counts. This corresponds to 104400±26300 counts per mole of barium sulfate. The error is determined by the variation in counts depending on the background subtraction method.

The sodium peak was obscured by the FeII peak (Figure 6). To fit the sodium doublet beneath the FeII peak, both elements were fit to the sum of three Lorentz line shapes (Equation 1),

$$y(\lambda) = D \cdot \left[\frac{A}{\pi} \cdot \frac{\gamma_{Na'}}{2} \cdot \left(\frac{1}{(\lambda - \lambda_{Na'}) + (\frac{\gamma_{Na'}}{2})^2} \right) + \frac{B}{\pi} \cdot \frac{\gamma_{Na''}}{2} \cdot \left(\frac{1}{(\lambda - \lambda_{Na''}) + (\frac{\gamma_{Na''}}{2})^2} \right) \right] + \frac{C}{\pi} \cdot \frac{\gamma_{Fe}}{2} \cdot \left(\frac{1}{(\lambda - \lambda_{Fe}) + (\frac{\gamma_{Fe}}{2})^2} \right) \quad (1)$$

where D is the relative integral of the sodium doublet, A, B, and C are the areas of each peak (A and B correspond to the two peaks in the sodium doublet, and C corresponds to the FeII peak), γ is the full width at half maximum of each peak, and λ is the peak center (λ'_{Na} is the peak center of the first sodium peak, λ''_{Na} corresponds to the second sodium peak, and λ_{Fe} corresponds to the FeII peak center).

The parameters fitting the sodium doublet were restricted to only vary the relative integral of the peaks D. The rest of the parameters, including peak center, peak width, and relative peak amplitude, were fixed based on the fit obtained from the experimental salt sample (see Section 3.6, Absolute Concentrations of Salt Composition). It is important to note that the peak areas A and B are coupled such that the ratio between A and B is constant, allowing for the relative peak integrals to be fixed.

The third term in the fit equation fit the FeII peak, and all parameters were left free to vary.

This Lorentz fit of the sodium doublet resulted in an integral of 386±150 counts. This corresponds to 30900±12000 counts per mole of sodium bismuthate.

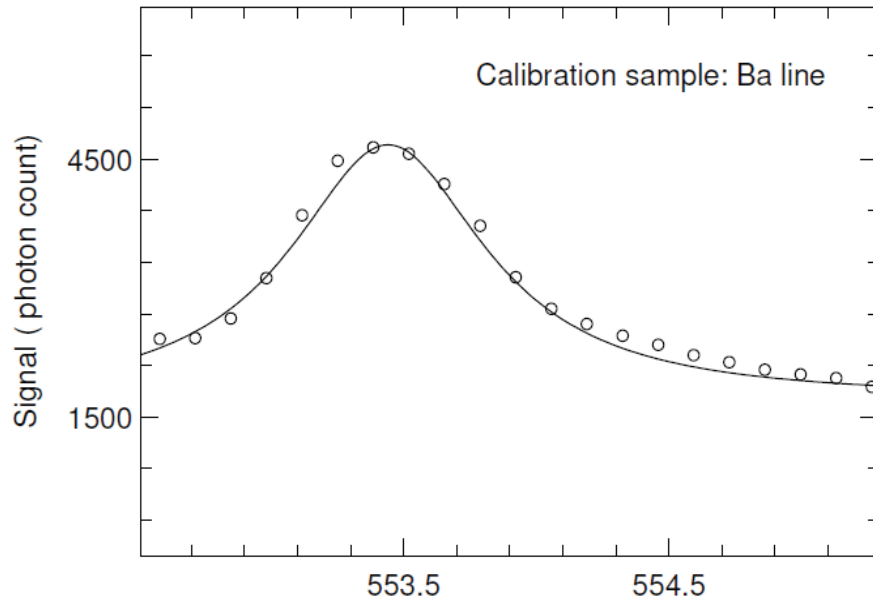From these fits it was determined that the barium peak intensity is 3.38±1.56 times that of the sodium doublet.

Figure 5: Lorentz fit (solid line) of barium peak in calibration (round circles are experimental data).
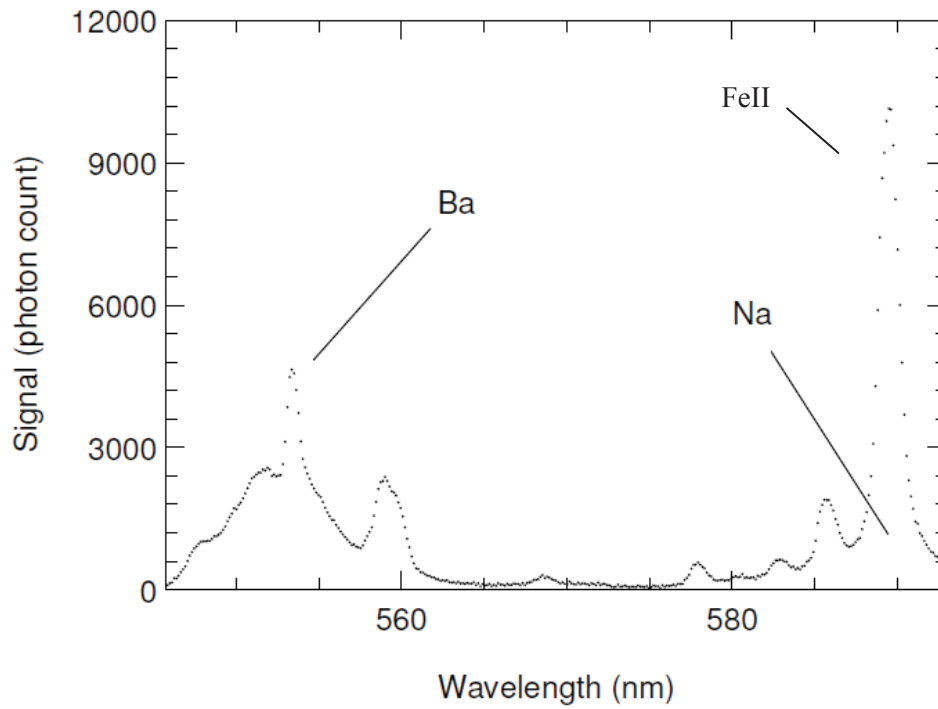

Figure 6: TRELIBS spectrum of calibration sample with additives of barium sulfate and sodium bismuthate. The sodium doublet is obscured by the iron peak.
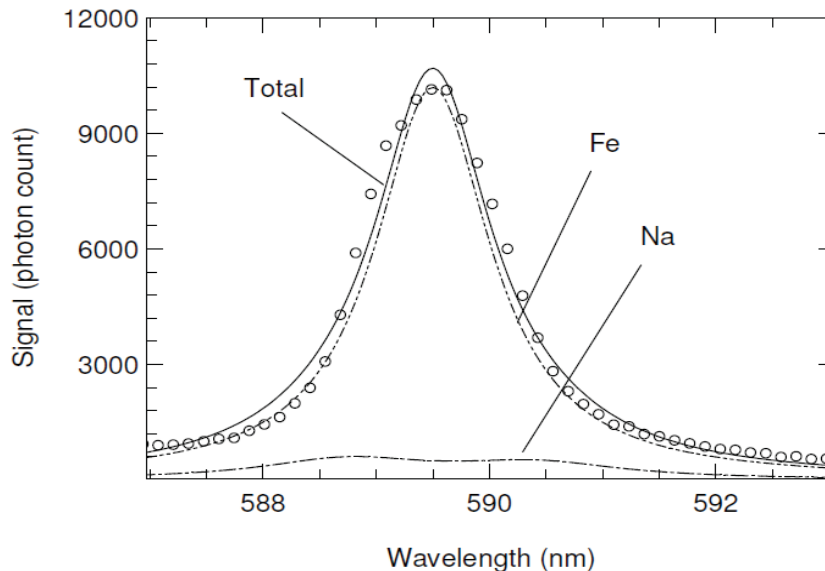
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Figure 7: Lorentz fit of experimental sodium doublet. Round circles indicate experimental data, small dashed line is the Lorentz fit of the Fe peak, large dashed line is the Lorentz fit of the sodium doublet, and the solid line is the total fit.

3.6   Absolute Concentrations of Salt Composition

In the salt sample, the barium and sodium peaks were fit with Lorentzian line shapes (Figure 8). The fits determined that the integrals of the sodium doublet and barium peaks were 585100 and 542±120 counts, respectively. Using the calibration from Section 3.5 (Calibration of Relative Intensities) it was determined that these relative intensities correspond to (0.28±0.06)% barium in the sample compared to sodium.

The primary form of the salt is NaCl, so it can be approximated that there is 50% sodium in the salt. Consequently, there would be (0.13±0.03)% barium distributed in the salt sample.

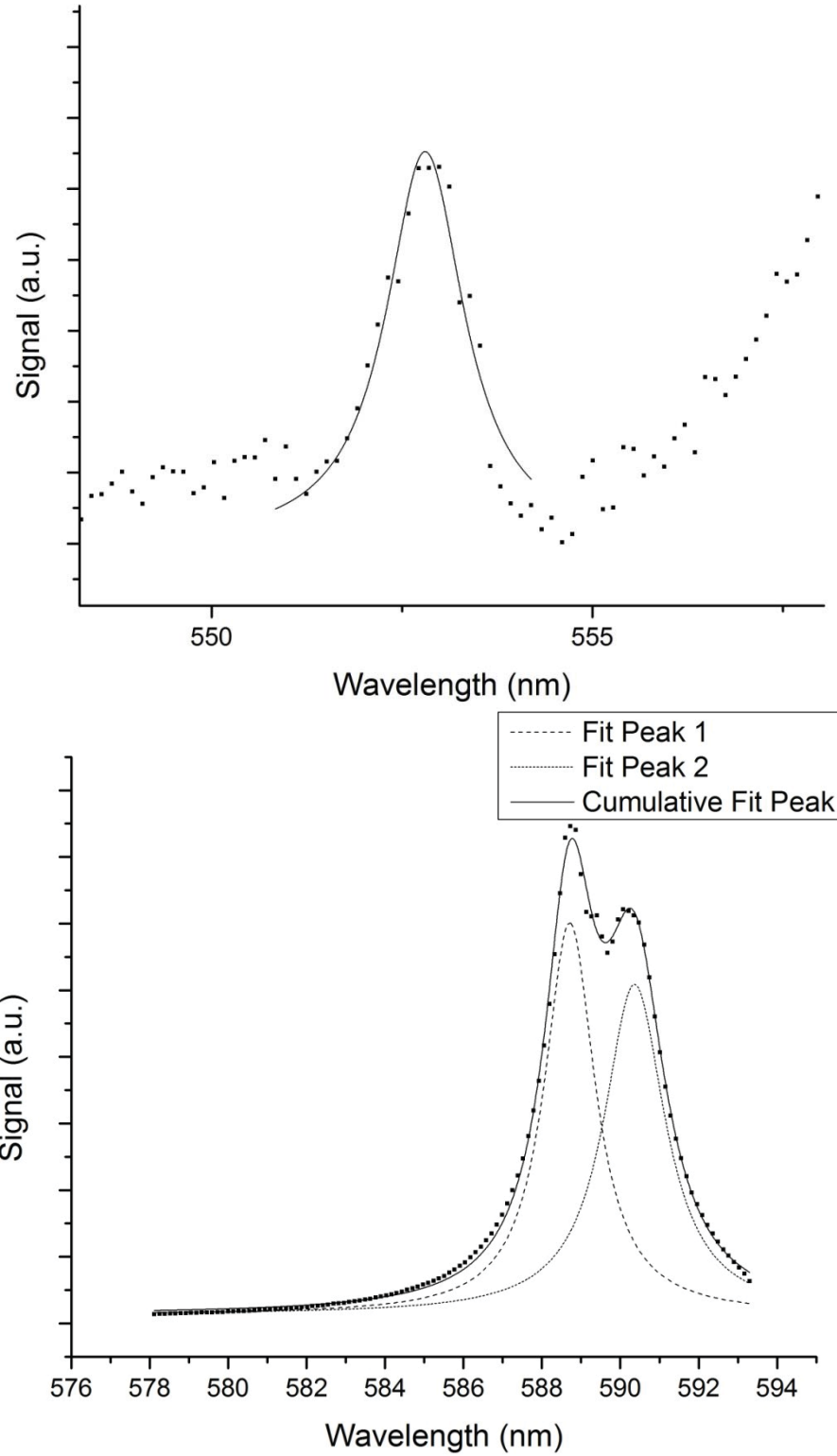While this uncertainty may seem large, it is accurate in the range of thousands of parts per million.

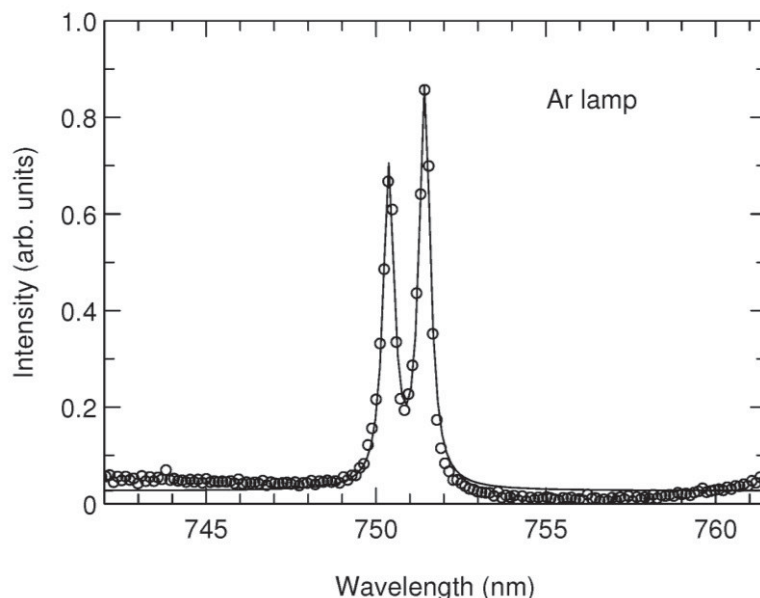**Figure 8: (top) Lorentz fit (solid line) of barium in salt sample. (bottom) Lorentz fit of sodium doublet.**

Figure 9: Spectrograph resolution determined by Argon lamp. Experimental data is indicated by the circles, and the data fit is indicated by the sold line.

3.7   Line Shape

In addition to the determination of the concentration of barium in the salt,

information about the nature of the TRELIBS plasma could be calculated based on the

spectra collected for the experiment. In this section, the reasoning for use of the Lorentz

line shape is presented and supported, and the pressure of the plasma is calculated based

on the line broadening of the spectral features.

The spectrograph resolution was determined by an argon lamp, which resulted in

a full width half maximum of 0.41nm (Figure 9). The argon emission was produced by a

low pressure, cold plasma, which would give a Doppler limited spectral line width of

0.002nm. Thus, the resultant broadening is purely due to the spectrograph resolution.

The line shapes in the TRELIBS spectra closely followed a Lorentzian profile

(Figure 8, bottom), and have a width significantly larger (1.9nm at FWHM) than the

spectrograph resolution. The Lorentz line shape suggests that the width is due to

collisional broadening [6]. This can be further supported by showing that the Doppler

width is small in comparison to the broadening observed. To calculate the Doppler width

of the sodium doublet, the temperature of the plasma needed to be determined.

Previous experiments in this laboratory (using the same laser and spectrograph)

determined the temperature of the TRELIBS plasma [11]. The background

bremsstrahlung continuum was observed, and the wavelength at maximum intensity was

measured at 340nm. By Weis's law, the temperature of the electrons was calculated to be

8500K. To account for differences between electron temperature and plasma temperature,

the continuum was observed near the end of its lifetime and the assumption was made

that at this time electrons had reached local thermal equilibrium with all other species.

The Doppler width of the sodium doublet was calculated using Equation 2 [6],

$$\Delta v_{doppler} = \frac{v}{c} \sqrt{\frac{8kTln(2)}{m}}$$

(2)

where $\Delta v_{Doppler}$ is the Doppler width at FWHM, v is the frequency at which the line

occurs, c is the speed of light, k is Boltzmann's constant, m is mass, and T is the plasma

temperature. It was determined that the Doppler broadening is 687GHz, or 0.007nm. This

width is much smaller than the observed broadening of 1.9nm.

Additionally, in Figure 10 it is clear that the tails of the sodium doublet do not fit

a Gaussian profile, which further confirms the width is not due to Doppler broadening.
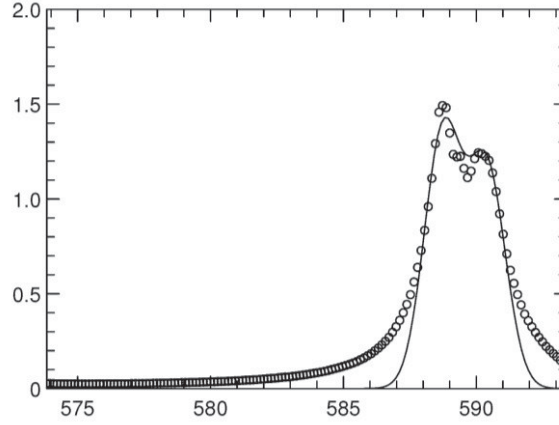
Figure 10: Sodium doublet from salt sample fit with a Gaussian profile (solid line).

The pressure of the plasma was calculated from the width of the spectral line at FWHM (Δv_{total}) (Equation 3a, 3b) [6].

$$\Delta v_{total} = \Delta v_n + \Delta v_{collisional} \cong ap_B \qquad (3a)$$

where Δv_n is the natural line broadening and the Doppler broadening (small compared to the collisional width), $\Delta v_{collisional}$ is the width due to collisional broadening, p_B is the pressure of the plasma, and

$$a = 2\sigma_{ij}\sqrt{\frac{2}{\pi\mu kT}} \qquad (3b)$$

where σ_{ij} is the cross section of the interaction, and μ is the reduced mass of colliding atoms. Here, the radius of the cross section is approximated as a hard-shell system where the atoms are roughly 5Å apart. μ is approximated from the assumption that most interactions occurring are between sodium and chlorine, and a reduced mass of 14.5 amu is used.

With these calculations, the pressure is determined to be ~680 atmospheres.

4   Conclusions

A salt sample from Hockley Dome in Texas was examined for barium concentration using TRELIBS. The TRELIBS setup was optimized with time delay and gate width of 15μs and 5μs, respectively. The relative intensities were converted to absolute concentrations using a homemade calibration sample. It was determined that the salt sample contains (0.13±0.03)% barium. This shows that it is possible to use this fast, field-ready technique in order to detect and quantify the trace concentrations of barium in rock salt.

5   References

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Appendix
Data Acquisition Design (DAD) Mode Protocol

Once triggered by the laser light, the OMA runs a customized Data Acquisition

Design (DAD) operation. The specific functions of the code are as follows:

- NORM 1024, which normally scans the 1024 channels

- The previous data is cleared from the memory data.

- PLSR 1303 Sets model number of the attached pulser.

- The Gate Pulse Interface 1303 is set to triggered mode pulsing.

- The 1304 Pulse Amplifier is designated as 'on'.

- The Data Precision is set to double precision (32-bit precision) for data
  storage.

- The Programmed Trigger is deactivated, meaning that there is no internal
  trigger and the trigger must come from the laser.

- Detector scanning synchronized to OMAVISION software.

- Time Delay and Gate Width are set.

- Multiple iterations are added into a single spectra.

The code clears the previous data from the memory, allowing for new data to

enter without becoming added to a different acquisition. The detector scanning is

synchronized to the OMAVISION software, and the Data Precision is set to double

precision (32-bit precision) for data storage. The Time Delay and Gate Width are set by

the user after optimization (see Section 3.2, Time Delay and Gate Width Optimization).

The DAD acquisition finally records data according to the Time Delay and Gate Width and adds multiple iterations into a single spectrum. The file is then written to a permanent file outside of the memory data.