Iron Measurement in Wastewater Outfall by Laser-Induced Breakdown Spectroscopy

C.R. Bhatt[1,2], Daniel Hartzler[1,2], Dustin McIntyre[1]

[1]National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26505, USA*

[2]NETL Support Contractor, 3610 Collins Ferry Road, Morgantown, WV 26505, USA*

Research & Innovation Center

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

Abstract

In this study, laser-induced breakdown spectroscopy (LIBS), in conjunction with principal component analysis (PCA) and linear discriminant analysis (LDA), was used to determine iron content in coal ash runoff. Wastewater was collected over a period of 10 days from the foundation underdrain of a building built on top of a coal ash base and was analyzed using a traditional LIBS benchtop system and custom LIBS probe. Spectra obtained from the test samples were compared to iron containing standards to identify the prominent iron emission lines as characteristic signatures. The strong atomic emission lines of iron at Fe I 371.9 nm and Fe I 373 nm were identified with the help of these standard samples, which demonstrated the significant presence of iron in the collected wastewater samples. Machine learning tools, PCA and LDA were used to classify the liquid samples by collection day. For quantitative study, partial least square regression (PLS-R) calibration curves were developed using the data collected from the reference samples and were used to estimate the iron concentration in the wastewater samples. To evaluate the accuracy of the results obtained, they were compared with inductively coupled plasma-mass spectrometry (ICP-MS) measurements, and the results were found comparable with relative difference below 15%.
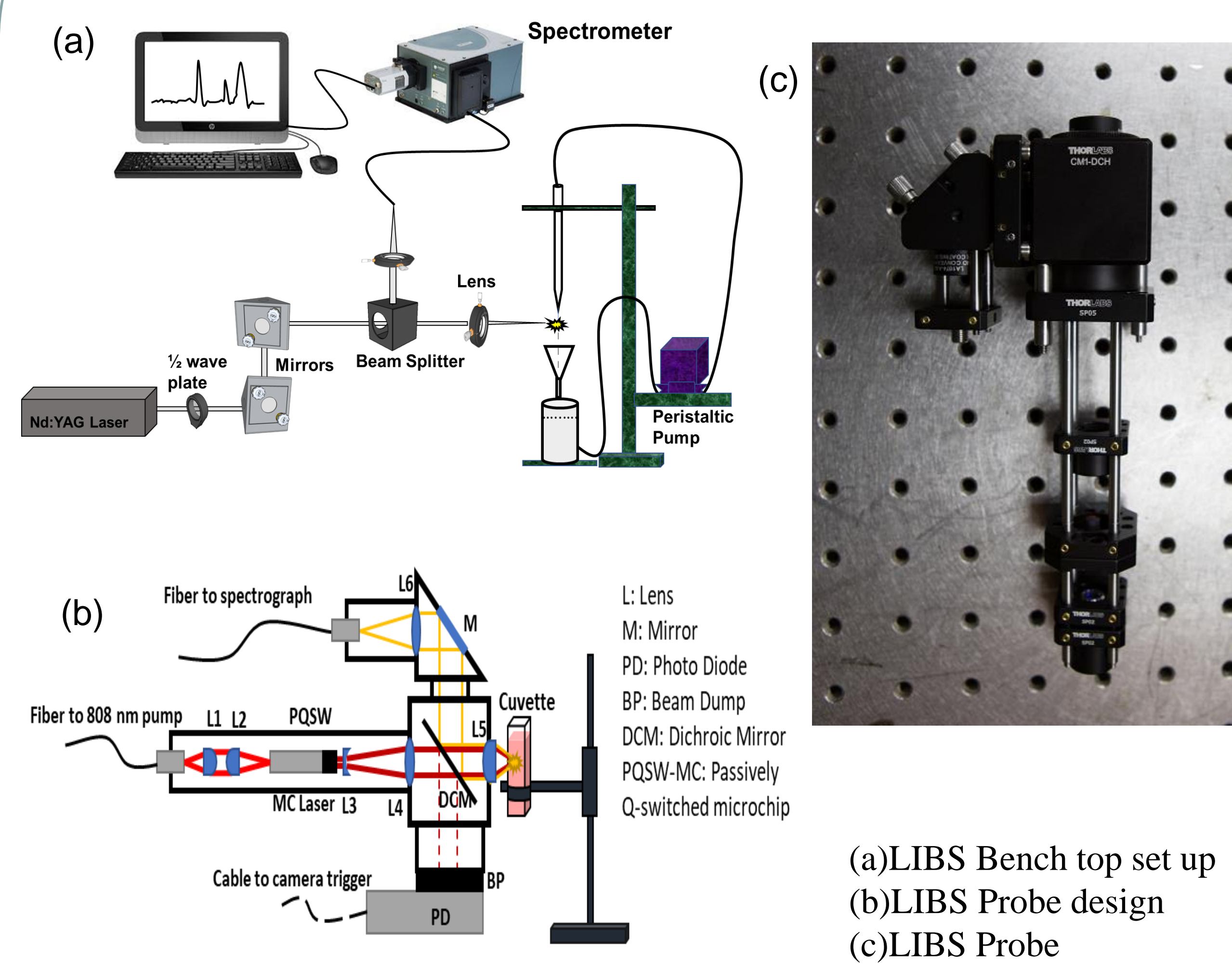
Laser Induced Breakdown Spectroscopy

* LIBS is an atomic emission spectroscopy-based analytical technique to obtain qualitative and quantitative elemental information of the materials.
* High-energy laser pulse creates a micro plasma plume on the sample by ablating a very small amount of material.
* The ablated material dissociates into excited ionic and atomic species.
* The excited atoms/ions present in the plasma emit light at their characteristic wavelengths.
* Spectral analysis of the emission spectrum from the plasma is used to infer the elemental composition of the sample.
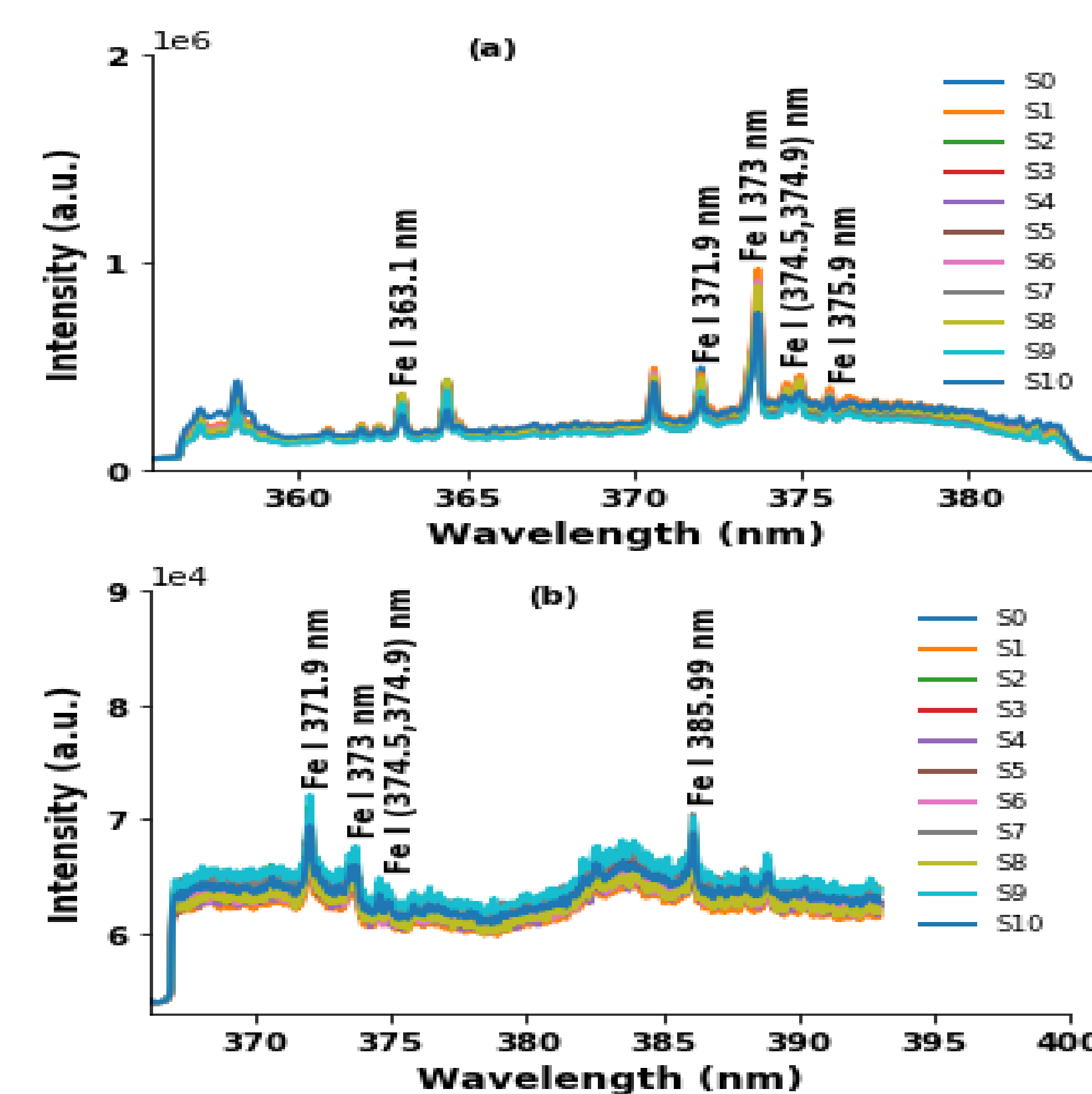
Materials

* Test samples named as S0, S1, S2, S3, S4, S5, S6, S7, S8, S9, S10 were collected from the waste-water outfall of one of the historic building at NETL Morgantown site.
* Sample S0 was collected on Dec 19, 2019 and samples S1-S10 were collected for 10 continuous days; Sept 29–Oct 8, 2020.
* To prevent the samples from precipitation, 10% by volume of nitric acid was added to all the samples.
* For calibration, a stock solution was prepared by dissolving $FeCl_2$ in DI water and nitric acid.
* Stock solution was further diluted to prepare calibration samples with Fe cation concentration range 1000 ppm–8 ppm.
* Univariate and multivariate calibration curves were developed from the LIBS data collected from calibration samples, which were later used to predict the iron content in the test water samples.
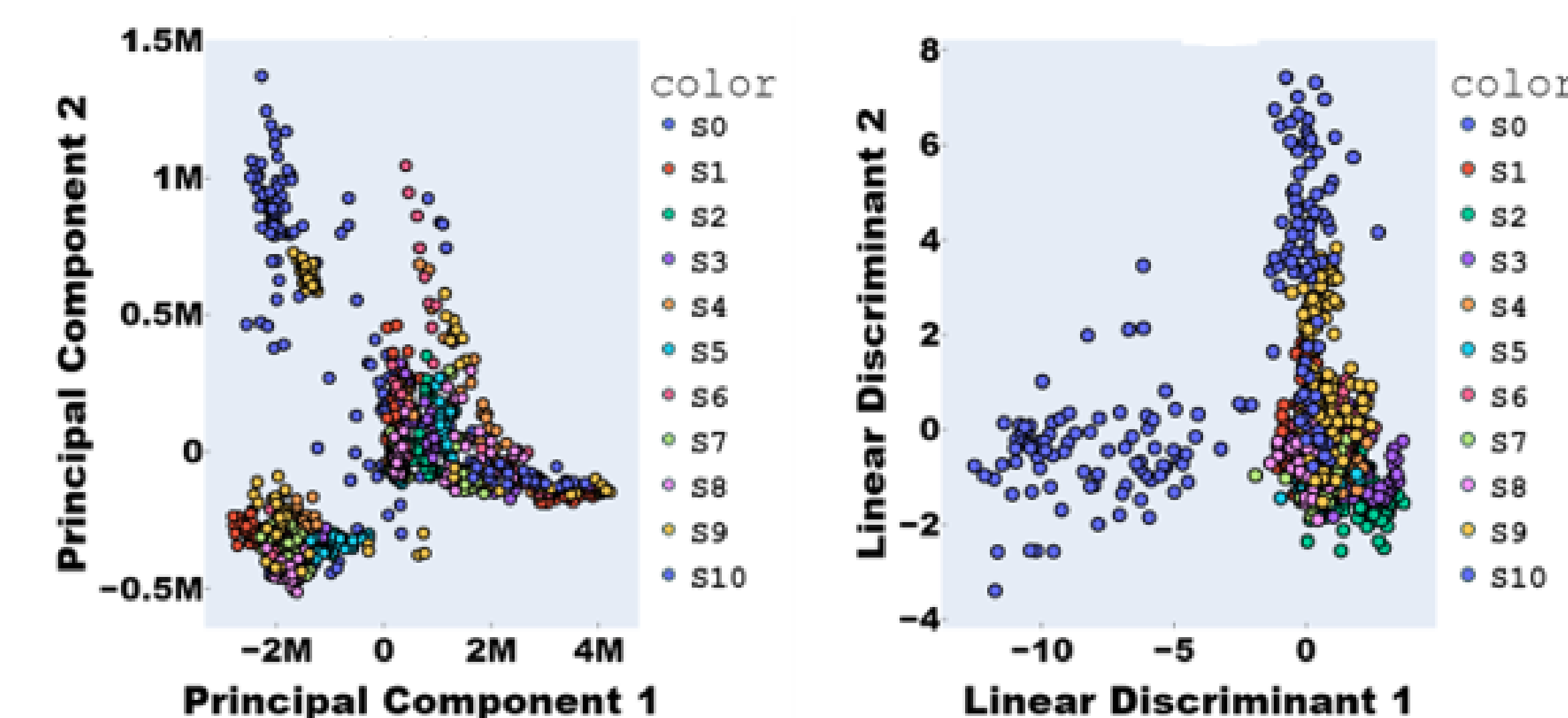
LIBS Detection Systems

(a)LIBS Bench top set up
(b)LIBS Probe design
(c)LIBS Probe

L: Lens
M: Mirror
PD: Photo Diode
BP: Beam Dump
DCM: Dichroic Mirror
PQSW-MC: Passively Q-switched microchip

Detection of Spectral Lines

Experimental Parameters		
	Bench top set up	LIBS Probe
Laser energy	15–30 mJ	4 mJ
Gate delay	1–5 μs	100–400 ns
Gate width	5–10 μs	0.5–3 μs
Wavelength	355–380 nm	360–390 nm

Fe lines detected in the spectra obtained using (a) LIBS benchtop set up, and (b) LIBS probe
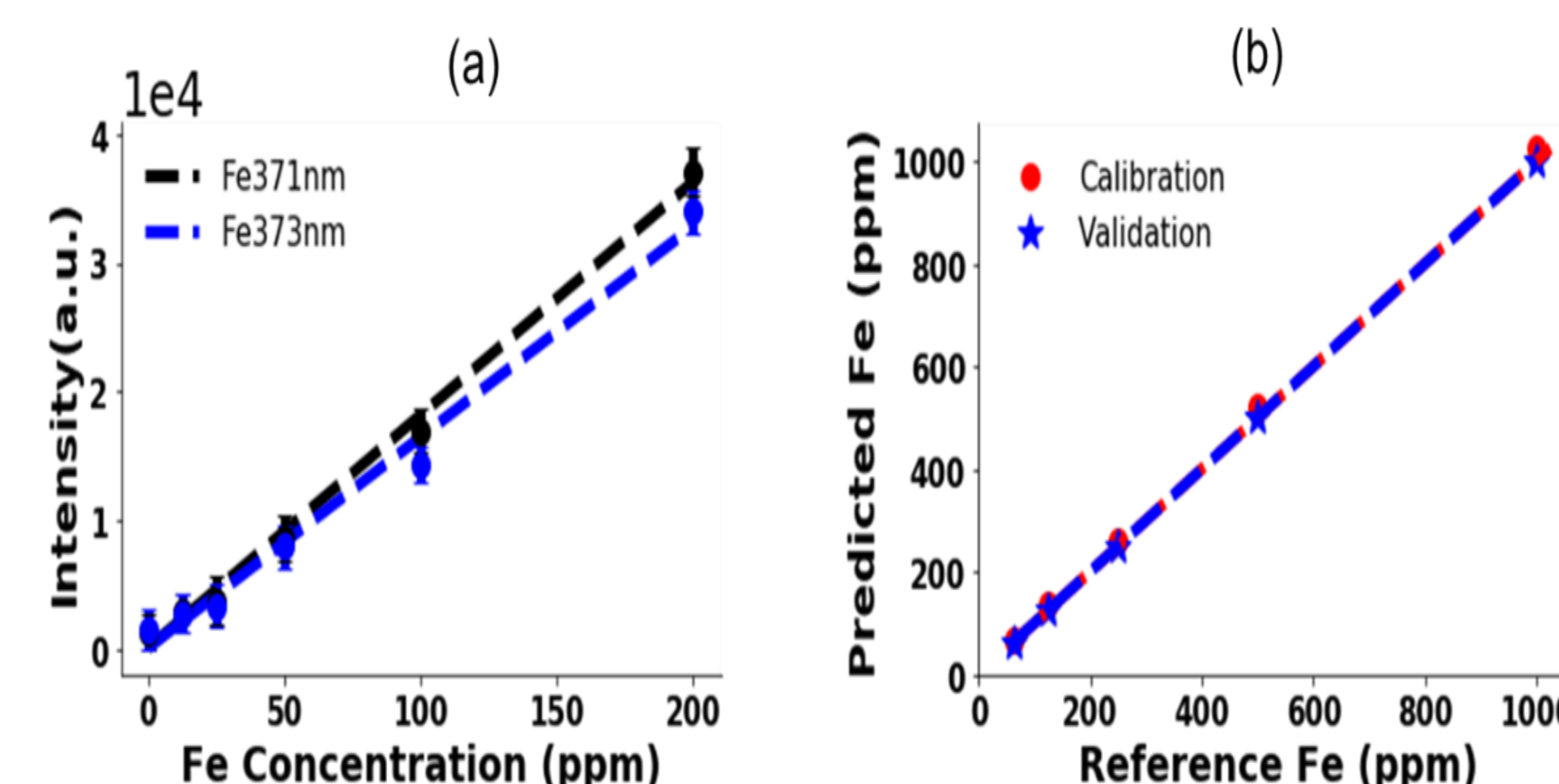
Principal Component and Linear Discriminant Analyses

(a) Scatter plot of first two principal components
(b) Scatter plot of first two linear discriminants

* PCA and LDA were combined to see clustering of the eleven water samples.
* PCA is an unsupervised machine learning method to reduce the dimensionality of large data sets, and it maximizes the variance of the data. It transforms a large set of variables into a smaller one, thus preserving most of the information held by original data.
* LDA is a supervised classification technique, and its goal is to project the features provided in higher dimensional space onto a lower-dimensional space.
* While PCA maximizes the variance of the data, LDA maximizes the distance between the groups of the data.
* LDA computes the directions called linear discriminants representing the axes, which maximizes the separation between multiple classes.
* Since the intensity values at different wavelengths are not independent, the data has collinearity issue. Therefore, PCA was performed first, and the principal components were used as input for the LDA. The individual principal components are always independent from each other, and linearity issue will be resolved. Ten principal components from PCA were extracted and used for LDA.
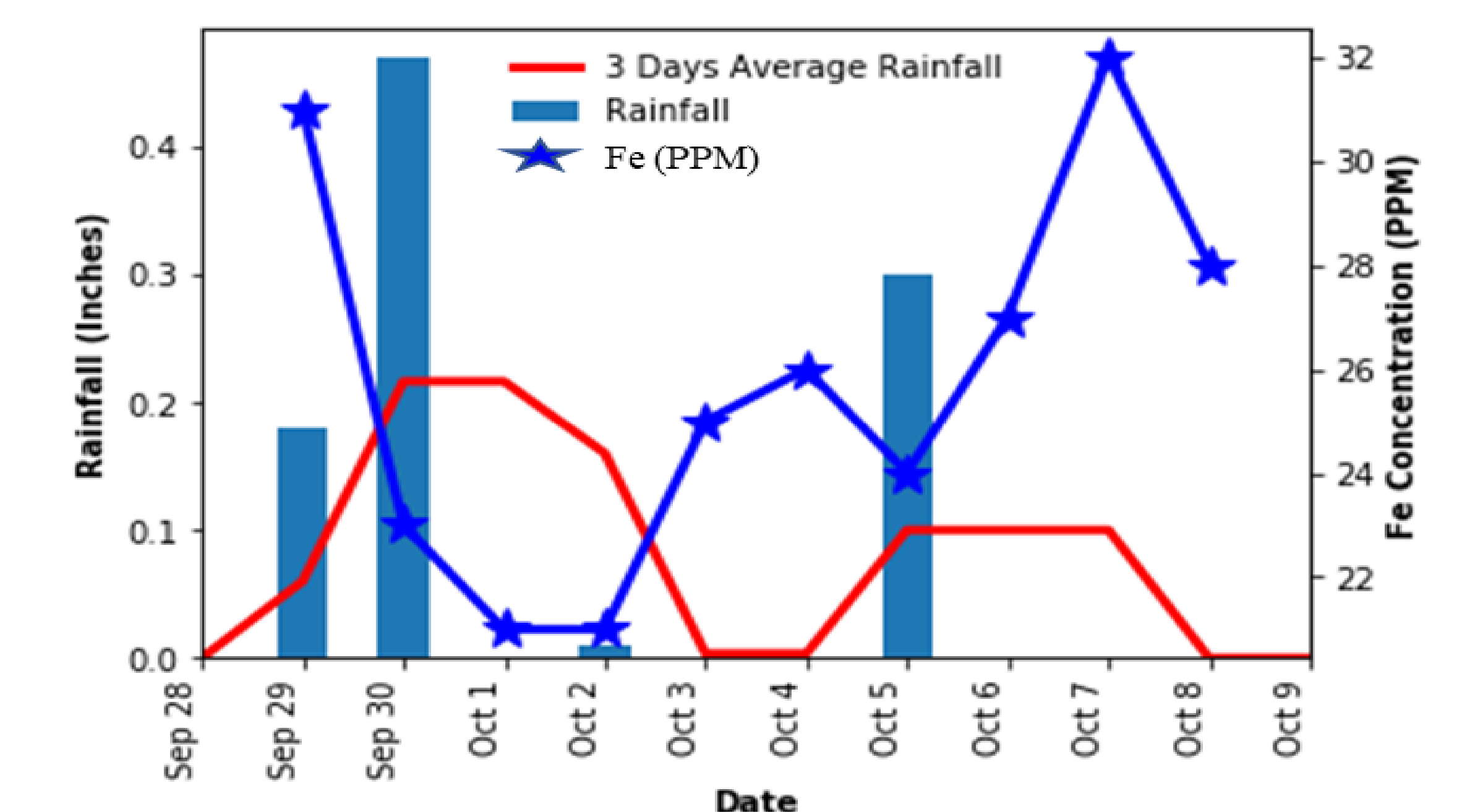
Quantification of Iron Content

(a) Univariate Calibration Curves
(b) PLS-R Calibration Validation Plot

Iron Concentration Measurements

Samples	Predicted Fe (ppm)		
	Univariate	Multivariate	ICP-MS
S0	34	32	28.60
S1	25	31	27.53
S2	27	24	23.05
S3	20	21	23.06
S4	21	21	24.41
S5	29	25	24.40
S6	28	26	24.35
S7	31	24	25.93
S8	25	27	24.86
S9	32	32	28.59
S10	28	26	24.70

Relative difference: PLS-R and ICP-MS <15%; ICP-MS and univariate analysis <20%.

Variation of Iron Content with Local Rainfall

A decrease in iron content was observed with the rainfall, which is likely due to the dilution of water with rainwater.

Conclusions

* LIBS appeared to be a very good analytical technique for iron content analysis in aqueous samples.
* Iron signals detected with benchtop set up: Fe I (363.1, 371.9, 373, 374.5, 374.9, 375.9) nm.
* Signals detected with LIBS probe: Fe I (371.9, 373, 374.5, 374.9, 385.99) nm.
* PCA and LDA showed that most of the samples were similar in terms of composition and concentration level.
* Iron content in the samples was found in 20–32 ppm range.
* LIBS and ICP-MS measurements have relative difference less than 20%.

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