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Rapid Nuclear Forensics Analysis via Machine-Learning-Enabled Laser-Induced Breakdown Spectroscopy (LIBS)

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Abstract. Nuclear forensics (NF) is an analytical methodology that involves analysis of intercepted nuclear and radiological materials (NRM) so as to establish their nuclear attribution. The critical challenge in NF currently is the lack of suitable microanalytical methodologies for direct, rapid, minimally invasive detection and quantification of NF signatures. Laser-induced breakdown spectroscopy (LIBS) has the potential to overcome these limitations with the aid of machine-learning (ML) techniques. In this paper, we report the development of ML-enabled LIBS methodology for rapid NF analysis and attribution in support of nuclear security. The atomic uranium lines at 385.464 nm, 385.957 nm, and 386.592 nm were identified as NF signatures of uranium for rapid qualitative detection of trace uranium concealed in organic binders and uranium-bearing mineral ores. The limit of detection of uranium using LIBS was determined to be 34 ppm. A multivariate calibration strategy for the quantification of trace uranium in cellulose and uranium-bearing mineral ores was developed using an artificial neural network (ANN, a feed forward back-propagation algorithm) and spectral feature selection: (1) uranium lines (348 nm to 455 nm), (2) uranium lines (380 nm to 388 nm), and (3) subtle uranium peaks (UV range). The model utilizing category 2 was able to predict the 48 ppm of uranium with a relative error prediction (REP) of 10%. The calibration model utilizing subtle uranium peaks, that is, category 3, could predict uranium in the pellets prepared from certified reference material (CRM) IAEA-RGU-1, with an REP of 6%. This demonstrates the power of ANN to model noisy LIBS spectra for trace quantitative analysis. The calibration model we developed predicted uranium concentrations in the uranium-bearing mineral ores in the range of 54–677 ppm. Principal component analysis (PCA) was performed on the LIBS spectra (200–980 nm) utilizing feature selection of the uranium-bearing samples collected from different regions of Kenya clustered into groups related to their geographic origins. The PCA loading spectrum revealed that the groupings of these samples were mainly due to rare earth elements, namely, cerium, dysprosium, praseodymium, promethium, neodymium, and samarium. ML-enabled LIBS therefore has utility in field NF analysis and attribution of uranium in NRM under concealed conditions.

INTRODUCTION

The illicit trafficking of nuclear and radiological materials (NRM), which began in the 1990s, has led to the emergence of a new branch of science known as "nuclear forensics" (NF) [1, 2]. NF is an analytical methodology that involves analysis of intercepted NRM so as to establish their nuclear attribution [3, 4]. The critical challenge in NF currently is the lack of suitable microanalytical methodologies for direct, rapid, and minimally invasive detection and quantification of NF signatures. Traditional analytical NF techniques (gamma spectroscopy, alpha spectrometry, mass spectrometry, profilometry, and electron microscopy) have limitations in this regard [1]. Laser-induced breakdown spectroscopy (LIBS), an emission spectroscopic technique, has several advantages over current NF techniques, namely, small sample size, direct analysis of inhomogeneous samples, minimal sample preparation, rapidity, and in situ analysis [5–7]. However, LIBS analysis is difficult in air and at atmospheric pressure because of the matrix effects arising from the strongly coupled transient laser–matter interactions [8]. As a result, most LIBS analyte spectral peaks are masked and buried by the strong background continuum. This limits the practical utility of LIBS in air at atmospheric pressure, in

addition to the interpretative challenges of the multivariate data [6, 8]. ML techniques have the ability to reduce the data and spectral dimensionality and to extract and model the subtle NF signatures to aid NF attribution [9].

METHODS AND MATREIALS

Laser-Induced Breakdown Spectroscopy

A Q-Switched Nd-YAG (Quantel Laser; Ocean Optics, Inc.) laser, delivering 50 mJ of maximum energy at a fundamental wavelength of 1064 nm and 10 Hz fixed-pulse repetition frequency, was optimized based on signal-to-noise ratio for the analysis of uranium in uranium trioxide (UO_3) and uranium-bearing mineral ores from different regions of Kenya pelletized in cellulose. When the 10-ns-wide laser is fired onto the sample, it ablates the sample surface and creates a microplasma. As the plasma decays or cools, the excited atoms in the plasma emit light of characteristic wavelengths specific to the elements present in the sample. The emission from the plasma plume was recorded by the seven HR2000+ high-resolution miniature fiber optic spectrometers placed at right angles to the direction of plasma expansion with a fused silica optical fiber (0.22 numerical aperture) of 101 mm focal length [9]. To ensure that all the information content of the pellet was absorbed, 50 spectra were collected from the different parts of the pellets and averaged to obtain a single LIBS spectrum.

A highly concentrated uranium pellet was prepared by mixing UO_3 in cellulose for qualitative analysis utilizing LIBS. The mixture was milled in a pestle using mortar for 30 min to achieve homogeneity and then pressed into 25-mm-diameter pellets of under a pressure of 10 tons using a hydraulic pellet press. Uranium pellets with concentrations ranging from 25 ppm to 800 ppm were prepared by mixing UO_3 with cellulose to develop a calibration strategy model for quantitative analysis of uranium. To validate the model, pellets with 280 ppm, 320 ppm, and 360 ppm of uranium were prepared by mixing CRM IAEA-RL-148 (400 ppm of uranium) with cellulose. Uranium-bearing mineral ores from different regions of Kenya were mixed with cellulose in the ratio 4:1 to prepare pellets for quantification of uranium levels and exploratory analysis.

Machine-Learning Techniques

ML is the study of techniques to automatically extract information from raw data [10, 11]. The goal of ML techniques is to solve a complex computational task by "letting the machine learn."

1. Principal component analysis (PCA). A central part in multivariate explorative data analysis, PCA is used to reduce data dimensionality while retaining the valuable information [12, 13]. In our study PCA executed using Unscrambler (Version 10.5) was utilized for data reduction and to find combinations of variables (principal components) to describe any significant patterns within the entire data set. The score of the individual principal components obtained from each PCA model described the variation in the samples in the data set, while loadings described the correlations among the variables [14].

2. Artificial neural network (ANN). To overcome the enhanced background, matrix effects, and nonlinearity of the noisy LIBS spectra, a multivariate calibration strategy using ANN coded in Matlab version 7.12 (The MathWorks, Inc.) was developed for quantitative analysis of uranium. A back-propagation algorithm was used because it allows the network to determine the best-fit training set of input–output pairs after a number of iterations based on gradient descent. The model was internally validated using the simulate samples of known concentrations of uranium (simulates that were not exposed to the model). The prediction accuracy of the model was tested using the CRM IAEA-RL-148. The relative error prediction (REP) was computed by using the following formula to determine the prediction accuracy of the model [15]:

$$\text{REP}(100\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\widehat{c_i}-c_i}{c_i}\right|, \text{REP}(100\%) = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{\widehat{c_i}-c_i}{c_i}\right|,$$

where N is the number of simulate samples in the dataset; c_i is the actual or reference concentration of the simulate samples; and $c_i \widehat{c_i}$ is the predicted concentration of the respective samples.

RESULTS AND DISCUSSIONS

The atomic uranium lines at 385.464 nm, 385.957 nm, and 386.592 nm were identified as NF signatures of uranium for preliminary investigations of trace uranium in concealed in organic binders and uranium-bearing mineral ores. The limit of detection of uranium using LIBS was determined to be 34 ppm. The uranium lines (atomic and singly ionized

uranium) identified in the pellet were categorized into weak, resonant, and interference lines. A multivariate calibration strategy for the quantification of trace uranium in cellulose was developed using ANN with spectral feature selection consisting of all the three categories of uranium lines and subtle uranium peaks. The model utilizing spectral feature selection was able to predict the concentration of uranium as low as 48 ppm with an REP of 10% and CRM concentration with an REP of 18%. However, the calibration model utilizing subtle uranium spectral features (category 2) could predict trace uranium in the pellets prepared from CRM with an REP of 6%. This therefore demonstrates the power of ANN to model noisy LIBS spectra for trace quantitative analysis. PCA performed on the LIBS spectra and by feature selection of LIBS spectra of uranium-bearing mineral ores collected from different regions of Kenya (North Ruri, South Ruri, Coast, and Lake Magadi) clustered into four groups, which related to their origins. The PCA loading spectrum revealed that the source attribution of the HBRA soil samples is mainly due to rare earth elements, namely, cerium (Ce), dysprosium (Dy), praseodymium (Pr), promethium (Pm), neodymium (Nd), and samarium (Sm). ML-enabled LIBS therefore has utility in field NF analysis and attribution of uranium in NRM.

CONCLUSIONS

LIBS has the potential to detect uranium in concealed condition. The unique NF signatures observed in the LIBS spectra can be used to detect the presence of uranium in unknown samples bound in a cellulose matrix. The calibration strategy model developed in ANN using LIBS spectra can quantify trace uranium concentrations in unknown samples, while PCA applied to LIBS spectra can establish patterns that relate to their attribution. Thus, ML-enabled LIBS can be developed to detect NRM under concealed conditions at stand-off distances. Such analysis will enable us to quantify trace concentrations of NRM and to retrace their origin, thereby strengthening the nuclear security of the country.

ACKNOWLEDGMENTS

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