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PAPER

Determination of isotope ratios using Laser-Induced Breakdown Spectroscopy in ambient air at atmospheric pressure for nuclear forensics

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Laser-Induced Breakdown Spectroscopy (LIBS) is currently a subject of great interest in spectroscopy and is being considered for the design of a field portable unit for nuclear safeguard inspection, because it allows a high level of portability and versatility while identifying the elements and materials of interest. Field portable technologies and methods are sought to provide simple, inexpensive, and fast analysis of materials in the mining, construction, and other industries. However, the level of portability needed for this particular application imposes some restrictions on the choice of many of the core components used in a low cost LIBS handheld sensor. This means that relatively low-performance components, such as a low-energy laser source and a low cost, low resolution spectrometer, must be considered to fulfil these conditions. In addition, the market price of such a portable device should be as low as possible to increase the breadth of potential end users and allow the deployment of multiple units for security enhancement. The present paper describes the determination of isotope ratios using Laser-Induced Breakdown Spectroscopy in air at atmospheric pressure for partially resolved uranium-235/uranium-238 and hydrogen/deuterium isotope shift lines in such conditions. Using a Partial Least Square (PLS1) regression, it is possible to build a model that enables the accurate determination of the isotopic ratio under conditions where the application of traditional univariate approaches for hydrogen and uranium would not be achievable without the use of ultra high resolution spectrometer. In addition, the application of PLS1 regression to determine the uranium-235/uranium-238 and deuterium/hydrogen isotopic ratios between 0 and 1 mass fraction was also successfully demonstrated. The performance obtained with such a LIBS sensor configuration demonstrates the possibility of integrating all of the required components in a small portable handheld system.

Introduction

The International Atomic Energy Agency (IAEA) has the mandate to safeguard the use of uranium, plutonium and thorium worldwide, for the purpose of preventing the diversion of these elements into the fabrication of weapons of mass destruction. From a non-proliferation standpoint, the uranium enrichment process is considered to be one of the most sensitive stages of the nuclear fuel cycle. For civil power generation, the amount of uranium-235 required to initiate and maintain the nuclear fission varies from 0.7 (natural) up to 4.5% (m/m), depending on the reactor type.¹ In general, a level of enrichment above 4.5% (m/m) can be considered to be intended for military

applications. A handheld device used in a complementary access campaign that can predict low isotopic enrichment of uranium will be a formidable tool for safeguarding the civil use of uranium.

Currently, isotopic determination is performed using high resolution gamma spectroscopy,² thermal ionization mass spectrometry³ or by inductively coupled plasma-mass spectrometry (ICP-MS)⁴ in a laboratory environment. These analysis techniques provide the sensitivity and selectivity required for the accurate determination of the different isotopes. However, the miniaturization of these techniques significantly compromises the analytical figures of merit and does not eliminate the need for sample preparation (*e.g.* ICP-MS). The gamma-ray spectroscopy systems (*e.g.* HM-5) offer the highest level of portability for complementary access inspection. These devices are very helpful tools for many safeguard applications, providing accurate and sensitive determination of the uranium-235 enrichment. However, the time required (up to one hour) to realize a measurement on a weakly enriched uranium sample currently limits their usefulness. IAEA inspectors presently use swipe sample kits to detect small traces of plutonium, thorium or

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uranium, which are then sent to a laboratory for analysis. This method provides very accurate results, however, it is very time consuming and burdensome, given the number of swipes taken by each inspector worldwide. A portable sensor that could perform rapid analysis with little or no sample preparation would allow inspectors to analyze many samples quickly, improving their ability to locate and identify suspicious materials. Moreover, such a device would allow improving the representativeness of the swipe sampling for politically sensitive samples that require additional analysis with a reference method.

Laser-Induced Breakdown Spectroscopy (LIBS) is currently a subject of great interest for security and forensic applications because of its high portability, instant results and adaptability.⁵ However, the level of portability needed for this particular application imposes some restrictions on the choice of many of the core components used in a low cost LIBS handheld sensor unit. This means that low-performance components, such as a low-energy laser source and a low cost, low resolution spectrometer, should be considered to fulfil these conditions. In addition, the market price of such a portable device should be as low as possible to increase the breadth of potential end users and allow the deployment of several units for security enhancement. In the present work, we describe the possibility of predicting different isotopic ratios using constraints imposed by a handheld LIBS sensor configuration under air at atmospheric pressure.

Pietsch *et al.* were the first to demonstrate the possibility of predicting the uranium-235 to uranium-238 ratio using LIBS under medium vacuum (0.03 mBar) using a high resolution spectrometer (resolving power $\approx 85\,000$).^{6–8} Winefordner *et al.* have shown the possibility of determining the 2 atomic mass unit (amu) isotopic shift of rubidium-85/rubidium-87 using Laser Ablation-Laser Atomic Absorption Spectroscopy in low vacuum (10 to 200 mBar) using argon as a support gas.⁹ Soon after, Smith *et al.* reported the detection of the 3 amu uranium-235/uranium-238 shift using LIBS coupled to Laser-Induced Fluorescence under medium vacuum (0.01 mBar).¹⁰ More recently, Smith *et al.* have shown the baseline resolution of the 6 pm isotopic shift for 1 amu of plutonium-239/plutonium-240 using a very high resolution (resolving power $\approx 300\,000$) with low vacuum (130 mBar) using helium as the support gas.¹¹ The baseline resolution for the hydrogen-1 to hydrogen-2 (*i.e.* deuterium) isotopic shift was reported recently by Kurniawan *et al.* using different helium pressures in different materials including water and heavy water.^{12–14} D'Ulivo *et al.* have determined the deuterium/hydrogen ratio in gas reaction products (headspace) directly inside a closed reaction vial.¹⁵ Probably due to a high level of Stark broadening of the H_α line, they showed that Lorentzian spectral deconvolution approach is limited to the determination of molar fraction difference between 0.5 and 1 (hydrogen : deuterium) of headspace gas (*i.e.* HD and H_2) resulting from the hydrolysis reaction of inorganic compounds.¹⁵ So far, these pioneering works have revealed the possibility of determining isotopic shifts using LIBS along with the use of vacuum and/or helium as the support gas, minimizing both Doppler and Stark broadening, thus enabling the baseline resolution of small isotope shifts using high resolution spectrometers. The work of D'Ulivo *et al.* is, to the best of our knowledge, the first attempt to predict the isotopic ratio without baseline resolved conditions.¹⁵ Their approach revealed good predictive ability, but it is limited

to the determination of molar fraction between 0.5 and 1 (hydrogen : deuterium).

The use of collinear signals—spectra defined by several sensors (*e.g.* pixels)—to resolve spectral interference has been investigated first for spectrophotometric analysis of multicomponent mixtures using multivariate statistics for quantitative measurement with the Beer–Lambert law.¹⁶ Multivariate techniques such as multiple linear regression (MLR), principal component regression (PCR) and partial least square (PLS) have been shown to be useful when coupled with LIBS for quantitative purposes.^{17–21} Recently, the use of low-resolution LIBS and chemometrics for quantitative analysis of organic materials has demonstrated that a low-resolution spectrometer (resolving power ≈ 700) can be used for quantitative measurements along with the information supplied by a laser-induced plasma.¹⁹ The present study investigates the possibility of determining the uranium-235/uranium-238 and hydrogen/deuterium isotope shift using partially resolved signals in air at atmospheric pressure. At present, to the best of our knowledge, nobody has yet reported the determination of isotope ratios in air at atmospheric pressure using LIBS. This is mainly due to the Doppler and Stark broadening effects which are considerable in these conditions, therefore making the baseline resolution of two different isotopes difficult without the use of spectrometer with a very high resolving power and vacuum with support gas conditions. Furthermore, under certain conditions, the Stark broadening of hydrogen and deuterium lines is large relative to the spectral separation, making them nearly impossible to resolve, irrespective of the resolving power. The present paper reports the successful and accurate determination of the isotopic ratio using partially resolved emission spectra.

Experimental

Apparatus and materials

The NRC-IMI/LIBS prototype 1 was used for the LIBS measurements. Briefly, prototype 1 was equipped with a Nd:YAG laser (Quantel, Big Sky CFR 400, Les Ulis, France) operating at the fundamental wavelength of 1064 nm at 2 Hz with 10 ns pulse duration. The pulse energy was fixed at 100 mJ with a 300 μm spot diameter (fluence $\approx 20\text{ J cm}^{-2}$) for solid samples, and 240 mJ with a 300 μm spot diameter (fluence $\approx 50\text{ J cm}^{-2}$) for liquid samples. The focal length of the laser focusing optics was approximately 75 cm (standoff distance). As configured, the light from the generated plasma plume was imaged onto the circular end of an optical fiber bundle (comprised of 25 individual fibers of 100 μm core diameter). The other end of the bundle takes the form of a 3 mm high by 100 μm wide stack of fibers, which acts as the slit of a 0.55 m Czerny–Turner spectrometer (Triax 550, Jobin Yvon-Horiba group, Kyoto, Japan). The spectrometer could be equipped with either a 2400 gr. mm^{-1} (resolving power $\lambda/\Delta\lambda = 11\,600$ @ 656 nm for 3 pixels) or a 3600 gr. mm^{-1} grating ($\lambda/\Delta\lambda = 20\,800$ @ 424 nm for 3 pixels), and was attached to an intensified charge-coupled device camera (Andor Technology, iStar DH-720, Belfast, Northern Ireland). The camera intensifier gain was found to be optimal at a value of 150. The detector timing was optimized at the beginning of the experiment. A delay of 20 μs with respect to the laser pulse and

an integration time of 2 μ s were found to give the best isotope shift resolution for U-235/U-238, while a 5 μ s delay and 1 μ s integration were found to be the optimal conditions for hydrogen/deuterium.

The experimental setup and spectral data were controlled using a custom application developed in LabVIEW 7.1 (National Instruments, Austin, TX, USA). Spectral data post-processing with chemometrics was performed using a custom algorithm under the Matlab 7.10 environment (The MathWorks Inc., Natick, MA, USA). All of the Matlab chemometric algorithms have been developed by NRC-IMI. All multivariate regressions use an iterative PLS1 algorithm.

Sample preparation

The following enriched uranium standards were kindly provided by the Safeguard Analytical Laboratories (SAL) of the International Atomic Energy Agency (IAEA), Seibersdorf, Austria. All standard solutions were prepared using pure water with 18 megaohm cm resistivity and nitric acid 65% (Pro Analysis, Merck, Germany). All of the solid samples were freshly prepared using 70 μ L of a dilute nitric acid solution of the different uranium enrichments (0.7, 3, 20 and 93% (w/w) U-235) at a concentration of 15 mg mL⁻¹ deposited on a ceramic sample holder and oven dried. Hence, a well controlled mass of a sample (e.g. 1.05 mg of U) could be deposited in the 1.5 cm² cavity of ceramic sample holder. Each solid sample was scanned 3 times, by firing 100 laser shots at 100 distinct positions each time. A single laser shot per position was taken on the sample surface, resulting in a total of 300 laser sampling points for each sample. The amount of ablated material is estimated to be around 500 picograms per pulse.

For hydrogen and deuterium, pure water with 18 megaohm cm resistivity and deuterium oxide, D₂O (99.9 atom% D, CDN Isotopes, Canada, Lot # E162P1), were used to prepare 0, 20, 40, 60, 80 and 100% (v/v) solutions of D₂O in pure water. The analysis was carried out by forming the plasma on the surface of a vertical, free falling liquid jet. Samples of 100 mL were circulated through the sampling system. A peristaltic pump fed the liquid into the opening of a funnel, which eliminated oscillations in flow, and the plasma was formed on the liquid jet several millimetres below the exit of the funnel. A series of five replicate measurements were taken on each sample, with one measurement consisting of 100 laser shots.

Results and discussion

Determination of the uranium-235/uranium-238 isotope shift

LIBS analysis was performed on 3 different uranium enrichment standards, after setting up optimized LIBS analytical conditions to improve the selectivity of the uranium isotopic shift at 424.437 nm, and the obtained LIBS spectra are presented in Fig. 1. Each pulse (1 spectrum) typically samples a few hundreds of nanograms. In contrast to the LIBS spectra reported by Pietsch *et al.*,^{6–8} the use of air at atmospheric pressure along with a resolving power of 20 800 ($\lambda/\Delta\lambda$ @ 424 nm for 3 pixels) prevented baseline resolution of the isotopic shift of the uranium ionic line from 424.437 nm (U-235) to 424.412 nm (U-238). Nevertheless, it is possible to observe the isotopic shift for 3

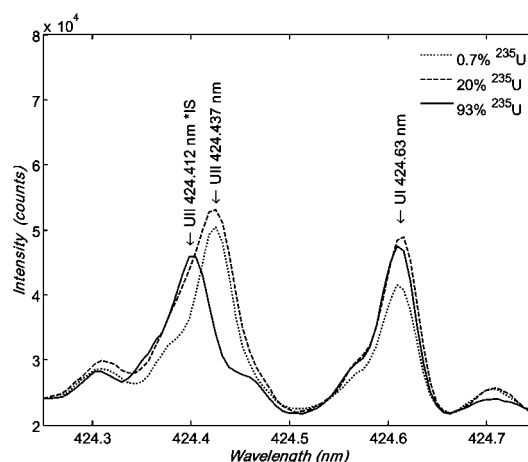


Fig. 1 LIBS spectra obtained for 3 different levels of uranium enrichment in air. *IS: stands for Isotope Shift.

different levels of U-235 enrichment without the use of a very high resolution spectrometer (resolving power \approx 85 000) under medium vacuum (0.03 mBar).^{6–8} It is also important to note in Fig. 1 that the atomic line of uranium at 424.63 nm is not affected by the enrichment in U-235 isotope.

A Partial Least-Squares (PLS1) model was built using the LIBS spectra from freshly prepared dilute nitric acid solutions of different uranium enrichment standards (0.7, 3, 20 and 93% (w/w) U-235 isotope). Each uranium enriched sample was analyzed by 100 laser shots for 3 replicates. The PLS1 model validation procedure was a cross-validation using 10 iterations with a block size of 3 (*i.e.* removing 3 standards randomly). The corresponding accuracies, in terms of percentage relative error, for the validated model are listed in Table 1. It is possible to see the good performance of the PLS1 over 3% U-235 which led to the accurate prediction of the U-235 isotope. The acceptable accuracies obtained demonstrate the selectivity of the PLS1 model using 3 latent variables for the uranium-235 isotopes. For natural uranium (0.70% U-235) up to 3% enrichment in U-235, the level of accuracy is between 6 and 8%, which can be considered acceptable for a handheld instrument to be brought on site for alert notification or to improve the representativeness of the sample taken on site. It is important to note that single shot analysis is possible at the cost of the precision of the results. Typically, the precision will be in the range from 3 to 10% depending on the enrichment level, which is compatible for use as an alarm instrument in complementary access inspection.

Table 1 Performance evaluation of the PLS1 model using 3 latent variables of the mean centered data

U-235 concentration (%)	PLS1 predicted concentration (%)	Relative accuracy (%)
0.70	0.760	8
3.0	3.19	6
20	20.5	3
93	92.9	0.1

Since enrichment of 4.5% in uranium-235 generally represents the limit between peaceful and rogue uses of uranium, the level of accuracy obtained is judged to be acceptable. In order to improve the level of accuracy, a higher resolution spectrometer would need to be used. The level of resolution used in the present work is considered to be near the lowest resolution acceptable to achieve accurate uranium enrichment prediction using the current PLS1 approach. The time required for analysis of low enrichment uranium is less than a minute, which is excellent compared to the several minutes required using a low resolution gamma spectrometer (*e.g.* HM-5).

Determination of the hydrogen/deuterium isotope shift

The LIBS spectra obtained for the analysis of different concentrations of D₂O (*i.e.* 0, 60, 100%) are presented in Fig. 2. It is possible to observe significant broadening of the H _{α} and D _{α} mainly due to Stark broadening.¹⁵ It is important to note here that a higher resolution spectrometer would not be able to resolve the H _{α} and D _{α} because of the experimental conditions. In fact, the water based plasma entails several spectroscopic challenges. First, the electron density of the laser-induced water-plasma is very high, resulting in a significant contribution of the Stark broadening of the hydrogen and deuterium lines, which already possess the highest line broadening coefficient of the periodic classification.²² In addition, the high concentration of hydrogen atoms in the plasma rapidly cools down the plasma due to the high thermal conductivity of the H/D atoms, leading to a short-lived plasma (*e.g.* less than 6 μ s).²³ Therefore, the time resolved conditions do not permit the use of a long delay in order to reduce the observed line broadening in the emission spectra presented in Fig. 2. The optimal time resolved conditions were found to be 5 μ s time delay and 1 μ s integration time. Taking into account the short life of the plasma, these conditions minimize the line broadening while maximizing the signal to noise ratio.

Obviously, a traditional univariate approach which relies on the peak height or peak area cannot be used in this case. In addition, the use of Lorentzian deconvolution has been shown to be limited due to the prediction of molar fraction of H : D

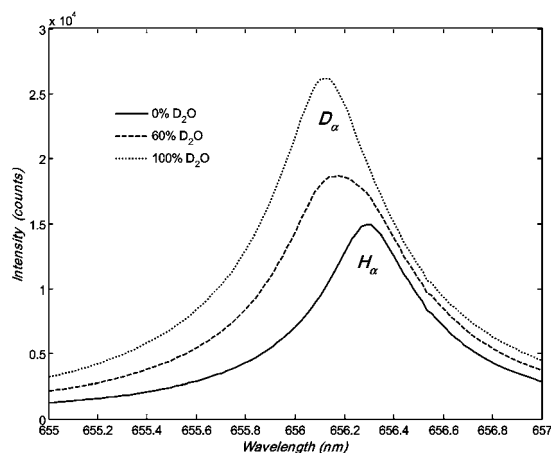


Fig. 2 LIBS spectra obtained for 3 different concentrations of heavy water in water, in air at atmospheric pressure for the optimal time resolved conditions (5 μ s time delay and 1 μ s integration time).

between 0.5 : 1 for H _{α} and D _{α} lines using better resolved peaks than those presented in Fig. 2.¹⁵ Nevertheless, the use of a multivariate regression technique has not yet been evaluated for quantitative analysis of elements by LIBS using poorly resolved lines as shown in Fig. 2. Since the spectrum of both pure components (*i.e.* H₂O and D₂O) has been acquired, the selectivity can be calculated using the Lorber, Bergmann, von Oepen and Zinn method denoted as the LBOZ selectivity.²⁴ Its possible value ranges between zero (complete spectral overlap of analytes and interferences) and unity (no overlap). The selectivity expressed in percent for D _{α} is 34% while the interference of H _{α} is the reminder since we have a binary mixture (*i.e.* 66%). Since the selectivity is different from zero, one can apply a multivariate regression to extract the information contained in the collinear overlapped signal. Therefore, a PLS1 regression model can correlate the spectral information contained in the LIBS spectra to the presence of heavy water in a binary mixture with water. The determination of an optimal number of latent variables is considered fundamentally essential for multivariate calibration, and can be evaluated by examining the plots of the root mean square error of calibration (RMSEC) and root mean square error of prediction (RMSEP) against the number of latent variables, shown in Fig. 3 for the PLS model for mean-centered data.

It is then possible to observe that the calibration error (RMSEC) and the prediction error (RMSEP) drop significantly beyond 3 latent variables. The RMSEP, which corresponds to the prediction error of the validation set, passes through a minimum at three latent variables before it rises again, as is often observed when building a PLS model. It is important to note that additional latent variables will start to include non-significant variation in the spectra, which will then increase the prediction error (*i.e.* RMSEP) since the regression model will start to model random noise and other non-correlated spectral data; this is typically referred to as over-fitting in chemometric terms. In theory, the number of latent variables expected should be the same as the number of independent variables, which is 2 in this case (*i.e.* H₂O and D₂O). However, in practice, it is often a few more than what the theory suggests, such that non-linear behavior of the signal and/or spectral interference can require

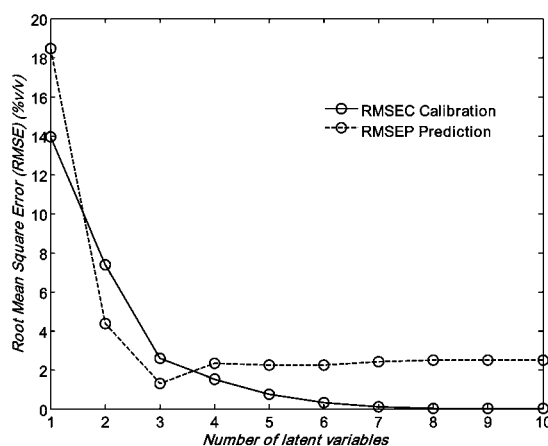


Fig. 3 Plot of the root mean square error of calibration and prediction, respectively, for the calibration and the validation set as a function of the number of latent variables considered in the partial least square model.

additional latent variables to build a reliable PLS model. The fact that the number of latent variables is 3 compared to 2 independent variables is a good indication of the validity of the developed PLS1 model of the mean-centered data. The plot presented in Fig. 3 clearly shows the optimal number of latent variables (*i.e.* 3), which suggests that the chemometric model is not presenting over-fitting of the data.

Validation of the PLS1 model for 3 latent variables is presented in Fig. 4 where the comparison between the predicted D₂O concentration by the PLS1 model and the prepared concentration for the calibration set and the validation set is shown. The 1 : 1 correspondence line shows the precise agreement between the predicted values and the prepared concentration. Globally for the calibration set and the validation set, the predicted values are in good agreement with the prepared concentration; the coefficient of determination R^2 is excellent with a noted value of 0.9988 and slope and intercept of 0.99 and 1.1 respectively. The relative accuracy calculated for each replicate of the validation set is presented in Table 2. Generally, the relative accuracy varies from 0 up to 3% of bias from the prepared value. The two first replicates (*i.e.* 20-R1 and 20-R2) present higher uncertainty than the rest of the validation set with 7 and 10% respectively. The validation sample 20-R2 has been tagged as an outlier using a median absolute deviation (MAD) base approach. MAD is to the median what the standard deviation is to the mean. In other words, MAD is an estimator of the spreading of the data in relation with the median of a population. Usually, a replicate that has an absolute standardized residual larger than 2.5 is flagged as an outlier. The absolute standardized residual (ASR) for a univariate population, x , can be calculated using the following equations:

$$\text{MAD} = 1.483 \text{ median}_i(|x_i - \text{median}_j(x_j)|) \quad (1)$$

$$\text{ASR} = (x_i - \text{median}(x))_i / \text{MAD} \quad (2)$$

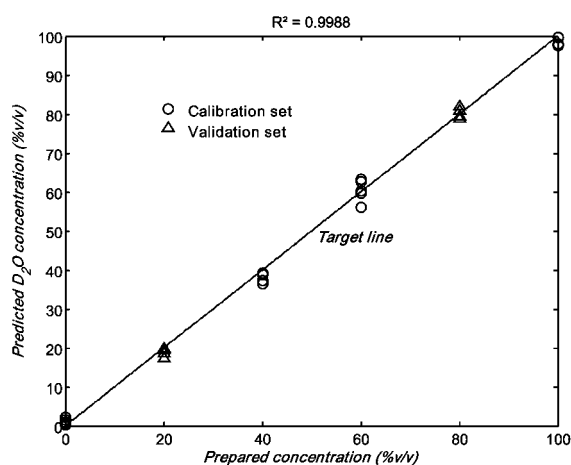


Fig. 4 Comparison between the predicted D₂O concentration by the PLS1 model and the prepared concentration for the calibration set and the validation set for the PLS model using 3 latent variables and mean centered data.

Table 2 Performance evaluation of the PLS1 model using 3 latent variables of the mean centered data

Validation standard name	Predicted concentration D ₂ O (v/v%)	Relative accuracy (%)
cc-R1 ^a	18.7	7
20-R2 ^b	17.4 ^b	10 ^b
20-R3	19.4	3
20-R4	19.8	1
20-R5	19.9	0
80-R1	78.8	1
80-R2	79.4	1
80-R3	81.1	1
80-R4	78.8	1
80-R5	82.1	3

^a "cc" stands for the D₂O concentration (v/v%) and "R1" the replicate number "1". ^b Outlier value determined by the absolute standardized residual larger than 2.5.

After removing the outlier, it can be stated that the predictive ability of PLS1 model for the prediction of the composition of a binary mixture of water and heavy water is excellent. This demonstrates the possibility of predicting the heavy water/water contents of a binary mixture using poorly resolved emission lines.

The analysis of explosive residues, or other organic, biological threats, on different surfaces is currently a hot topic in the LIBS literature since it implies many challenges.²⁵ In the case of chemical, biological, and explosive threats, the analytes are organic or bioorganic molecules composed of the same elements as the surfaces we can find in the real world (wood, polymer, paint, any combination of those, *etc.*).²⁵ Thus, when chemical, biological, and explosive traces are found on metallic surfaces, it is relatively "easy" to detect them.²⁵ However, the surrounding air is also composed of the same elements found in explosive residues.²⁵ In that respect, the case of uranium residues is not as challenging as it is for other chemical, biological, and explosive threats, but some difficulties may remain. It is important to note that all the measurements done in the present work are performed on synthetic samples. Therefore, the results reported in this manuscript are first to be viewed as a proof of concept of the underlying approach. Additionally, the analysis of actual samples coming from a country under investigation by the IAEA could be sensitive from a legal point of view. On the other hand, the selectivity challenges in the case of uranium traces are not the same. If someone detects uranium traces on a surface where you do not expect to find them, there is a potential problem. Uranium is found naturally in the earth crust, but with a low occurrence of 0.7% U-235. When the proportion of U-235 increases beyond this value, it is an indication of an artificial (man-made) enrichment process, and this is precisely where the concept brought in this manuscript could be useful to detect radiological threats. When uranium on a surface is analysed, the observed emission spectra are significantly different from spectra associated to any surface you can find in the real world, whether being made of steel, copper, nickel, titanium, zirconium, *etc.* Uranium and plutonium have several thousands of emission lines in the UV-VIS-NIR spectra; this brings a unique selectivity compared to explosive residues and other organic threats which are composed of the same elements (*i.e.* C, H, O, N, P, and S) found on most surfaces as well as in the ambient air in the real world. Moreover,

these elements are not rich in emission lines; they have less than a few hundred emission lines in the UV-VIS-NIR spectra. Therefore, the transition from synthetic to real samples is expected to be easier than it would be for other organic threats. In conclusion, additional measurements are required to demonstrate the validity of the approach presented in this manuscript for radioactive samples present on different surfaces.

Conclusions

Chemometrics coupled with LIBS is a suitable combination for the determination of isotope ratios in air at atmospheric pressure using poorly resolved lines. The use of the PLS1 technique that aids in the construction of the multivariate calibration model can accurately determine the uranium-235/uranium-238 and hydrogen/deuterium isotope ratios. The accuracy obtained for the determination of the uranium-235/uranium-238 isotope shift is considered suitable for a surface measurement which interrogates a few hundreds of nanograms of mass per pulse. In addition, the accuracy obtained for the determination of the hydrogen/deuterium isotope ratio is considered suitable for this application. The global performance of this approach is considered excellent for the rapid determination of the isotope ratio using a low weight portable LIBS sensor. LIBS can be considered as a valuable asset to the nuclear forensics toolbox. Finally, the results obtained show that the chemometric procedures used are robust enough to be integrated in a software user interface that can be accessed by non-qualified personnel for identification of materials.

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